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COLLABORATIVE STUDY OF METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES (FOSSIL-FUEL FIRED STEAM GENERATORS)

Henry F. Hamil, et al

Southwest Research Institute

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A collaborative study has been performed on Method 6 promulgated by EPA for determining the concentration of sulfur dioxide emissions from stationary sources. Method 6 specified the extraction of a gas sample from the stack, the separation of the sulfur dioxide from the acid mist including sulfurtrioxide, and the measurement of the sulfur dioxide fraction as sulfate by the barium-thorin titration method. Collaborative tests were conducted at both a coal-fired steam generating power plant and an oil-fired pilot plant by the same four collaborative teams. Satistical analysis of the collaborative test and associated data revealed the following findings regarding the reliability, both of a Method 6 determination, and of a Method 6 test result, which is defined as the average of six determinations: Accuracy : Method 6 is accurate in the SO_2 concentration range below 300c 10^{-7} lb/scf, but it acquires a significant 5- to 10% negative bias below the true conc. above 500 x 10^{-7} lb/scf. Precision: The estimated within-lab and lab bias standard deviations of a Method 6 determination are 4.0 and 4.2%, respectively, of its value. The repeatability standard deviation of a test result is estimated as 1.6% of its value. The estimated reproducibility standard deviation of a test result is 4.5% of its value. Minimum Detectable Limit: A conservative estimate of the minimum detectable limit of a Method 6 test is 2.1 x 10^{-7} lb scf. Sources of Reproducibility Variation: Most (75%) of the reproducibility variation in a test result resides in the field sampling phase of Method 6, with 25% occurring in the analytical phase. Only 13% reproducibility variance is caused by repeatability sources, while 87% results from lab bias sources.

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by

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ABSTRACT

A collaborative study has been performed on Method 6 promulgated by the Environmental Protection Agency for determining the concentration of sulfur dioxide emissions from stationary sources. Method 6 specifies the extraction of a gas sample from the stack, the separation of the sulfur dioxide from the acid mist including sulfur trioxide, and the measurement of the sulfur dioxide fraction as sulfate by the barium-thorin titration method. Collaborative tests were conducted at both a coal-fired steam generating power plant and an oil-fired pilot plant by the same four collaborative teams. Statistical analysis of the collaborative test and associated data revealed the following findings regarding the reliability, both of a Method 6 determination, and of a Method 6 test result, which is defined as the average of six determinations:

Accuracy–Method 6 is accurate in the SO_2 concentration range below 300×10^{-7} lb/scf, but it acquires a significant 5- to 10-percent negative bias below the true concentration above 500×10^{-7} lb/scf.

Precision–The estimated within-laboratory and laboratory bias standard deviations of a Method 6 determination are 4.0 and 4.2 percent, respectively, of its value. The repeatability standard deviation of a test result is estimated as 1.6 percent of its value. The estimated reproducibility standard deviation of a test result is 4.5 percent of its value.

Minimum Detectable Limit–A conservative estimate of the minimum detectable limit of a Method 6 test result is 2.1×10^{-7} lb/scf.

Sources of Reproducibility Variation–Most (75 percent) of the reproducibility variation in a test result resides in the field sampling phase of Method 6, with the other 25 percent occurring in the analytical phase. Only 13 percent of the reproducibility variance is caused by repeatability sources, while the remaining 87 percent results from laboratory bias sources.

Various modifications to Method 6 are suggested to improve its suitability for field compliance performance testing.

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I. INTRODUCTION

This report describes the work performed and results obtained on Southwest Research Institute Project 01-3487-001, Contract No. 68-02-0623, which includes collaborative testing of Method 6 for sulfur dioxide emissions as given in "Standards of Performance for New Stationary Sources."[1]*

This report describes the collaborative testing of Method 6 in a coal-fired steam generating power plant and in an oil-fired pilot plant, the statistical analysis of the data from the collaborative tests, and the conclusions and recommendations based on the analysis of data.

*Superscript numbers in parentheses refer to the List of References at the end of this report.

II. COLLABORATIVE TESTING OF METHOD 6

A. Collaborative Test Sites

Two collaborative tests of Method 6 were conducted. One test was performed at the Dayton Power and Light Company's Tait Station, Dayton, Ohio from February 5 to February 8, 1973. The second was performed at Walden Research Corporation, Cambridge, Massachusetts, from March 5 to March 8, 1973.

The first collaborative test was conducted at the Tait Station of Dayton Power and Light Company, Dayton, Ohio. Monsanto Research Corporation and Dayton Power & Light Company have an agreement permitting MRC to use DP&L's Tait Station (Figure 1) for investigation of various instruments and analytical methods for monitoring stationary combustion sources. A 10 X 14 ft utility shed was installed on the roof of DP&L's Tait Station between Units 4 and 5 (Figure 2). Units 4 and

Figure 1. Dayton Power and Light Company's Tait Station

5 are both tangentially fired, steam boilers burning pulverized coal. The only difference between the two units is that Unit 5 now has a set of mirror-grid electrostatic precipitators in operation in addition to the electrostatic precipitators employed on Unit 4. The maximum electrical output of each unit is 140 megawatts. The sample delivery line shown in Figure 2 is used to transfer the stack gas from a position after the electrostatic precipitator and before the induced draft fan to the MRC shed.

Inside the shed is a manifold for distribution of the flue gas. The manifold is 10 ft long, with an upper 2-in.-square duct fitted with 12 outlets and a lower 8-in.-square return duct (Figure 3). The sample delivery line was connected directly to the manifold for use on this test. The 2-in. black iron connecting pipe was wrapped with heating tape and insulated. The entire system is heated, and the temperature can be controlled by sections. Additional sample preparation capabilities include a Rotron Simplex spiral blower for supplying dilution air (Figures 3, 4, and 5).

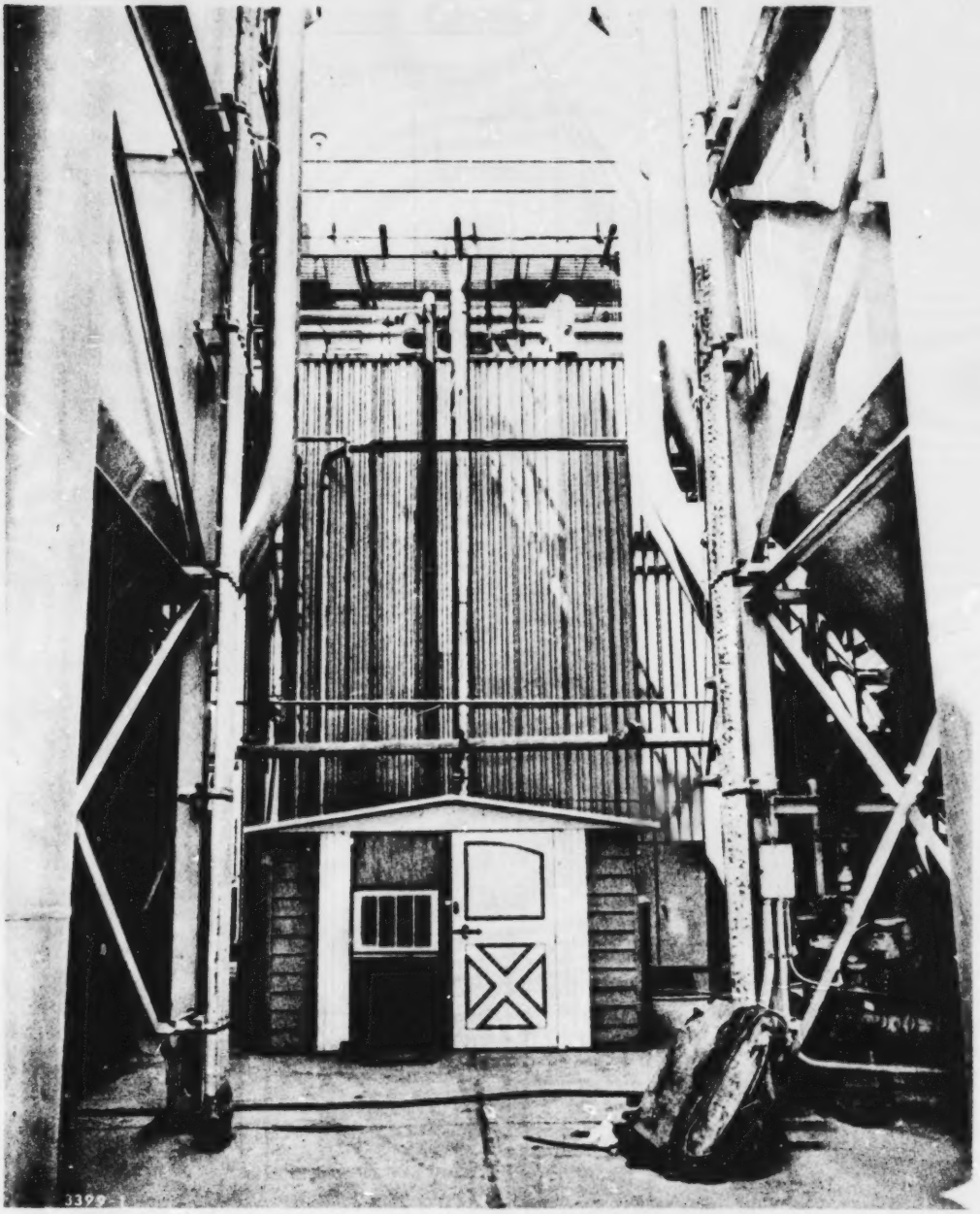

Figure 2. Test Facilities

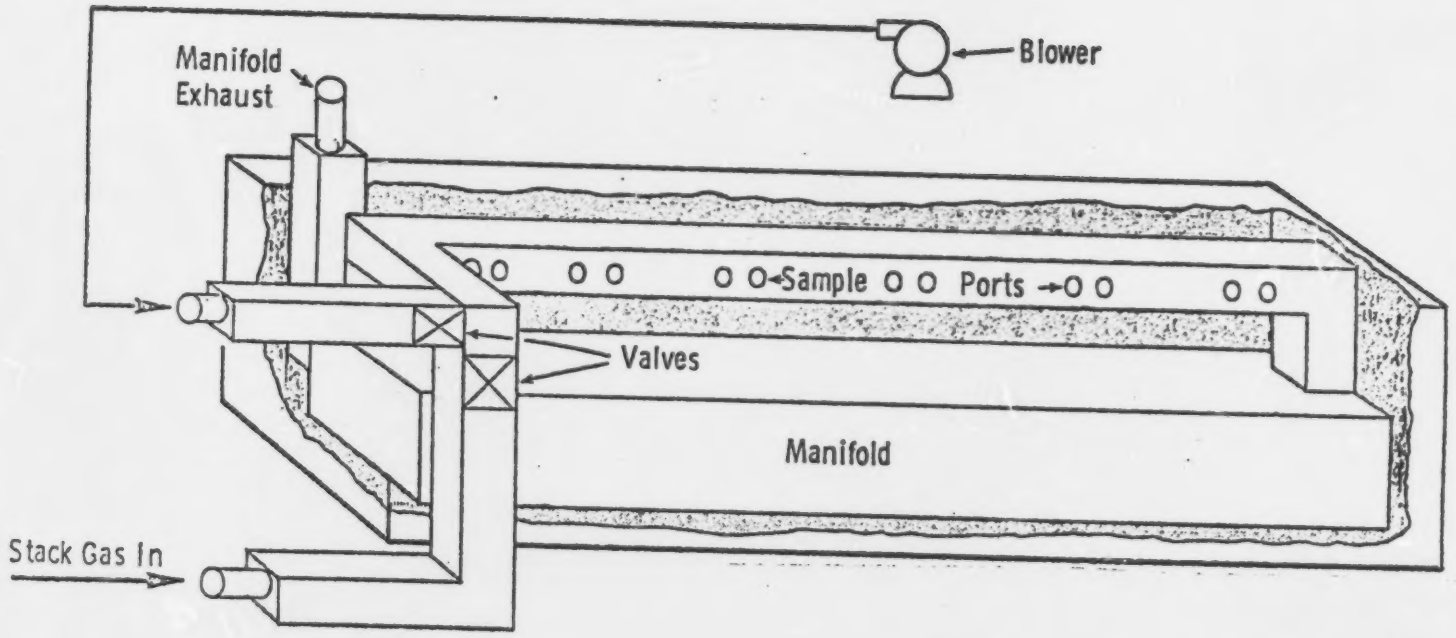

Figure 3. Stack Gas Delivery System and Sampling Manifold

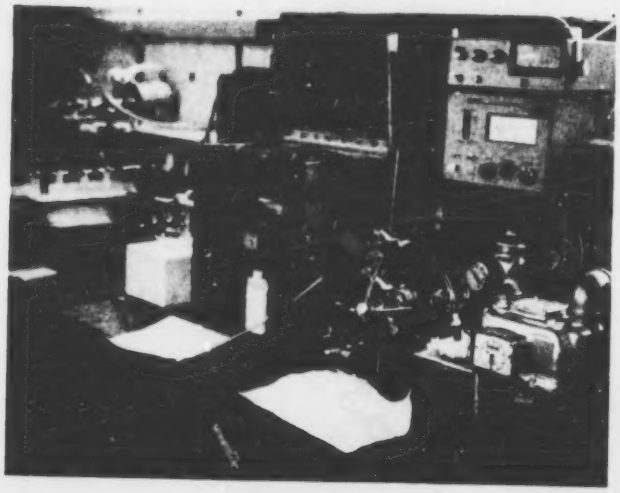

Figure 4. Sample Trains, Dayton SO_2 Collaborative Test

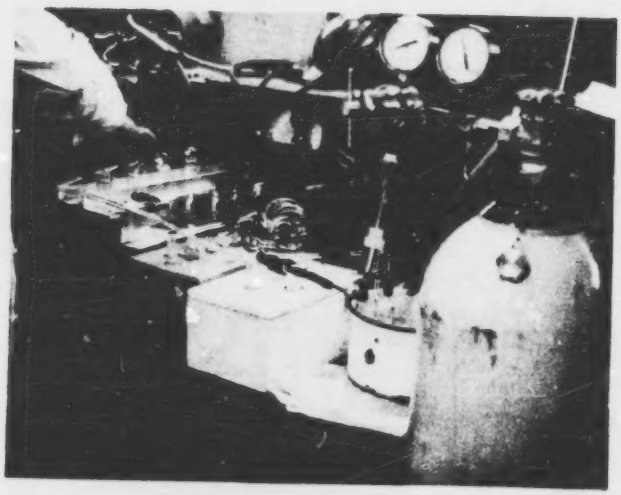

Figure 5. Gas Standard Sampling, Dayton SO_2 Collaborative Test

The installation of the Rotron Simplex blower allowed the addition of ambient air to dilute the stack gas to give different levels of sulfur dioxide during the collaborative test. Sulfur dioxide concentration in the stack gas and diluted stack gas was monitored with a calibrated Dynasciences instrument.

The second test was conducted on the Walden pilot plant. A schematic of the Walden combustion pilot plant is shown in Figure 6. The unit consists of a 400,000 BTU/hr (Jackson and Church) furnace with a combination gas/oil burner. The waste heat is discharged and the exhaust gas from the burner is passed into a series of carbon-steel test sections 3 ft in length and 8 in. in diameter. The flue gas is cooled down to about 300°F by an air-cooled heat exchanger and passed into a second series (3) of carbon-steel test sections (sampling areas). The gas is pulled out of these test sections by a Westinghouse induced-draft fan and exhausted through corrugated pipe at roof level.

On furnaces of this type, a thermal safety switch is incorporated in the burner shroud. It was planned to achieve different levels of SO_2 by firing the furnace on Nos. 2, 4, and 6 fuel oil. Accurate fuel feed rate measurements, along with fuel analyses and Orsat analyses, were to be used to calculate theoretical SO_2 levels in the flue gas. Due to unseasonably warm weather, when attempts were made to run with Nos. 4 and 6 fuel oil, the shroud overheated and the furnace shut down. Attempts to lower the heat output by decreasing the fuel feed rates led to unstable burner conditions and furnace failure.

Therefore, the decision was made to conduct the entire test using No. 2 fuel oil, with a known sulfur content, and to achieve the desired levels of SO_2 by doping the flue gas with accurately measured amounts of SO_2. By so doing, theoretical SO_2 levels could still be calculated for comparison with test data.

The gas doping system consisted of a 1A gas cylinder containing pure sulfur dioxide, glass rotameter (Fischer & Porter 448-209), and a simple toggle valve. The dopant gas stream is introduced into the high temperature section immediately after the fire box to come to equilibrium temperature and concentration across the duct before reaching the sample test section.

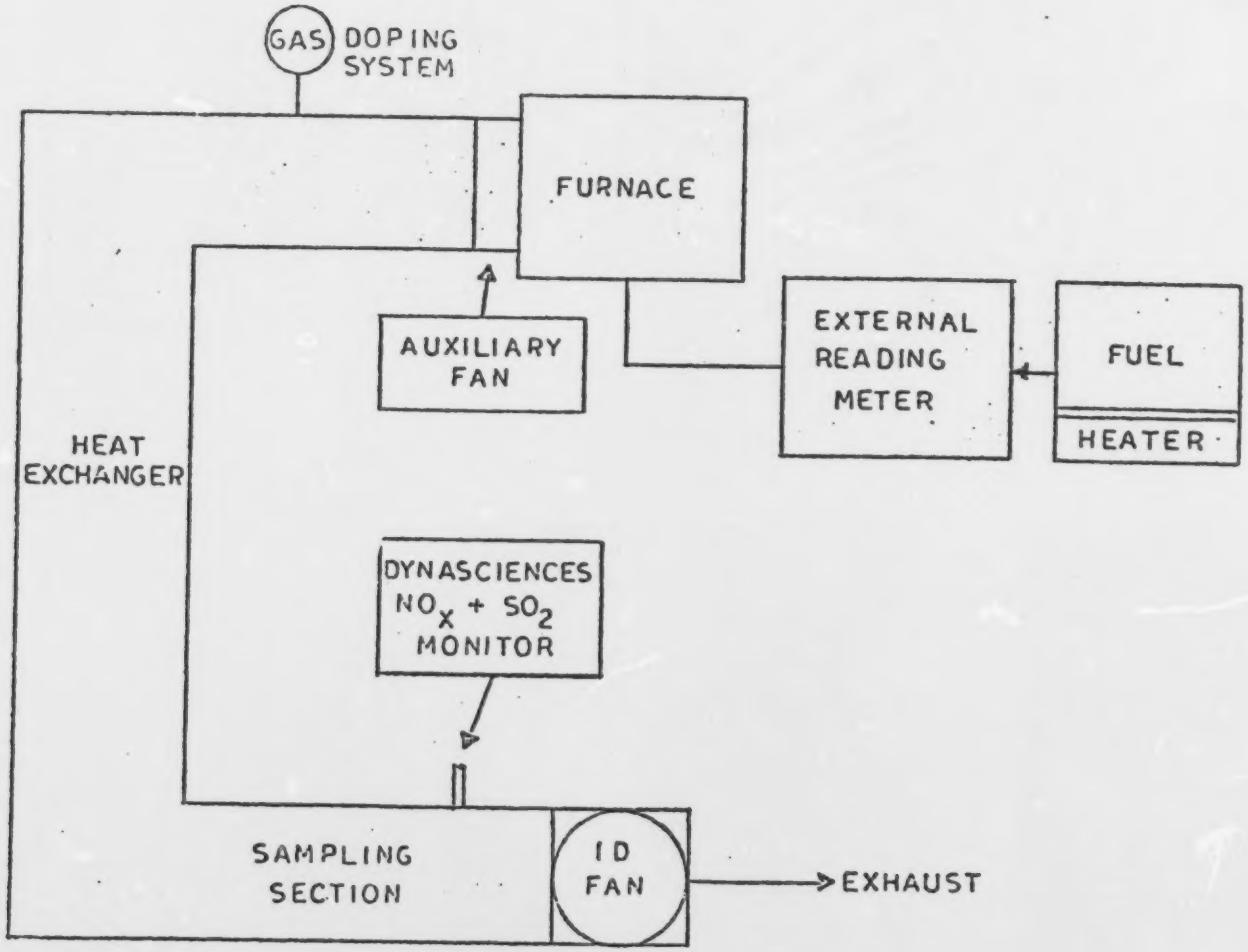

Figure 6. Pilot Plant Operational Configuration

The sample test section is shown in Figure 7. The sampling ports show both the earlier number code and the letter code, designated on December 12, 1972. The sampling probe was designed to be at the centroid of the duct, although the sample gas velocity profile is essentially flat across the duct.

B. Collaborators

The collaborators for both the Dayton and Cambridge tests were Mr. Rudy Marek (Dayton) and Mr. David Tarazi (Cambridge) of Southwest Research Institute, Houston Laboratory, Houston, Texas; Mr. John Millar of Southwest Research Institute, San Antonio Laboratory, San Antonio, Texas; Mr. James Becker of Walden Research Corporation, Cambridge, Massachusetts; and Mr. Paul Sherman of Monsanto Research Corporation, Dayton, Ohio. The latter two collaborators were under subcontract to Southwest Research Institute, and, in addition to serving as collaborators, had the responsibility for site preparation and test facility maintenance at their respective test sites. Throughout the remainder of this report, the collaborative laboratories are referenced by randomly assigned code numbers as Lab 101, Lab 102, Lab 103, and Lab 104. These code numbers do not correspond to the above ordered listing of collaborators.

Collaborative tests were conducted under the general supervision of Dr. Henry Hamil of Southwest Research Institute. Dr. Hamil had the overall responsibility for assuring that the collaborators were competent to perform the test, that the test was conducted in accordance with the collaborative test plan, and that all collaborators adhered to Method 6 as written in the *Federal Register*, December 23, 1971.

C. Philosophy of Collaborative Testing

The concept of collaborative testing followed in the tests discussed in this report involves conducting the test in such a manner as to simulate "real world" testing as closely as possible. "Real world" testing implies that the results obtained during the test by each collaborator would be the same results obtainable if he were sampling alone, without outside supervision, and without any additional information from outside sources, i.e. test supervisor or other collaborators.

The function of the test supervisor in such a testing scheme is primarily to see that the method is adhered to as written, and that no individual innovations are incorporated into the method by any collaborator. During the test program, the test supervisor observed the collaborators during sampling and sample recovery. If random experimental errors were observed, such as mismeasurement of volume of absorbing solution, improper rinsing of flasks, etc., no interference was made by the test supervisor. Since such random errors will occur in the every day use of this method in the field, unduly restrictive supervision of the collaborative test would bias the method with respect to the performance test results which will be obtained when the method is put into general usage. However, if gross deviations were observed, of such magnitude as to make it clear that the collaborator was not following the method as written, these would be pointed out to the collaborator and corrected by the test supervisor.

While most of the instructions in the *Federal Register* are quite explicit, some areas are subject to interpretation. Where this was the case, the individual collaborators were allowed to exercise their professional judgment as to the interpretation of the instructions.

The overall basis for this so-called "real-world" concept of collaborative testing is to evaluate the subject method in such a manner as to reflect the reliability, repeatability, and reproducibility of the method that would be expected in performance testing in the field.

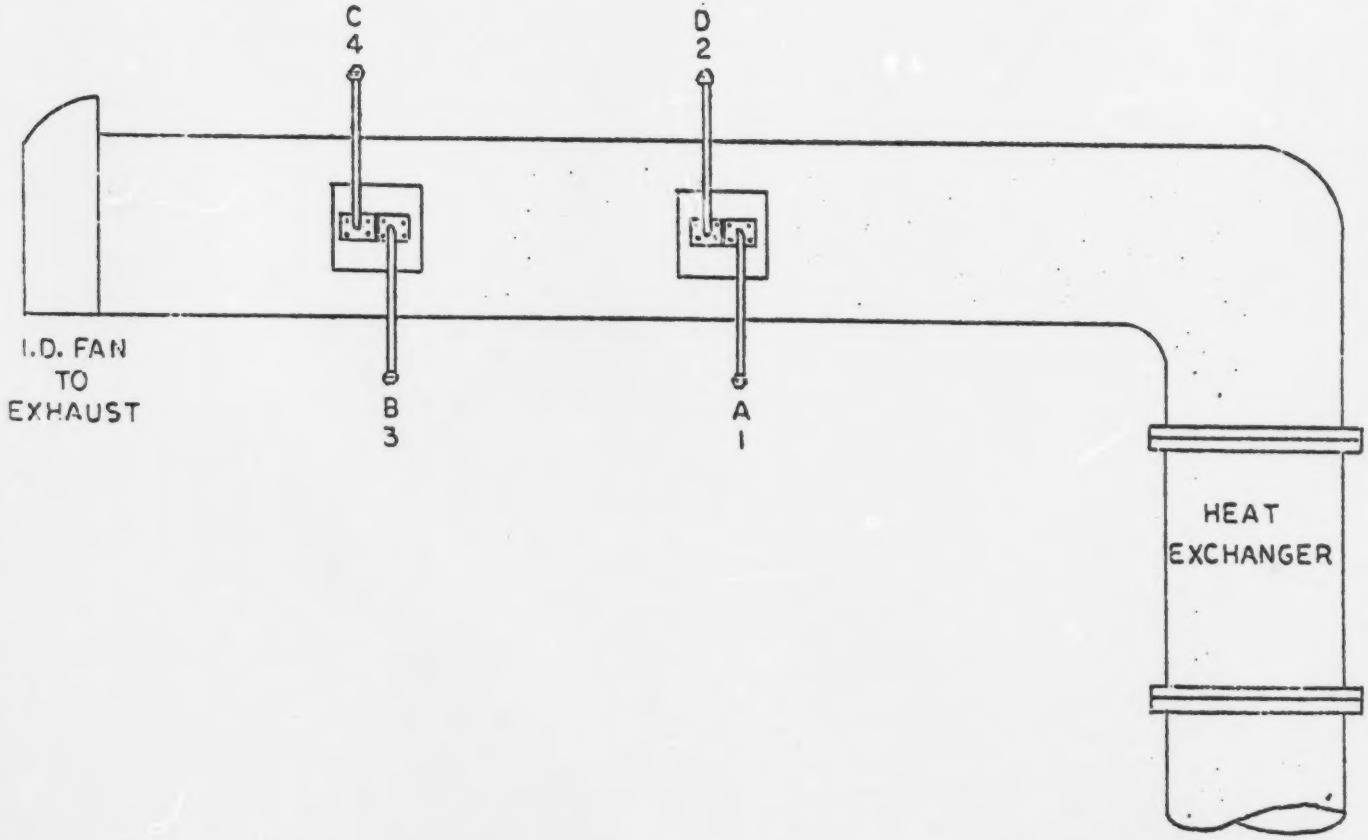

Figure 7. Top View of Test Section

III. STATISTICAL DESIGN AND ANALYSIS

A. The Experimental Design

A randomized block design was employed to collaboratively test Method 6 at both the Dayton site (Dayton Power & Light Company's Tait Station) and the Cambridge site (Walden Research Corporation's combustion pilot plant). Table 1 provides a schematic representation of the randomized block design utilized in the Dayton test. As this table illustrates, the Dayton test was conducted at four different blocks of emission concentration levels; these blocks had SO_2 concentration levels of about 840 X 10^{-7}, 580 X 10^{-7}, 175 X 10^{-7}, and 1090 X 10^{-7} lb/scf.* These blocks, each of which consisted of four runs sampled at 60-min. intervals, were obtained on consecutive days. The intent was to maintain a constant true SO_2 emission concentration level in the stack on the four runs within each block to permit an accurate determination of the repeatability precision of Method 6. Each run involved the simultaneous collection of an exhaust sample from the stack over a 20- to 23-min. interval by each of the four collaborative laboratory teams through their assigned port (A, B, C, or D). During the course of conducting each block's four runs, as Table 1 shows, the laboratory teams rotated systematically from port to port so that each team sampled once from each port. The systematic rotation facilitated the transfer of sampling apparatus between runs.

Table 1. Randomized Block Design of the Dayton Collaborative Test of Method 6

Block (concentration level), lb/scf	Run (sample)	Laboratory Team			
		Lab 101	Lab 102	Lab 103	Lab 104
~840 X 10^{-7}	1	B	C	A	D
	2	C	D	B	A
(2/5/73)	3	D	A	C	B
	4	A	B	D	C
~580 X 10^{-7}	11	C	D	B	A
	12	D	A	C	B
(2/6/73)	13	A	B	D	C
	14	B	C	A	D
~175 X 10^{-7}	15	D	A	C	B
	16	A	B	D	C
(2/7/73)	17	B	C	A	D
	18	C	D	B	A
~1090 X 10^{-7}	25	A	B	D	C
	26	B	C	A	D
(2/8/73)	27	C	D	B	A
	28	D	A	C	B

Notes: The letters A, B, C, and D denote the sampling ports to which each collaborative laboratory team was assigned on each run. The twelve sample numbers not listed here (5-10, 19-24) were obtained from standard gas cylinders in the gas cylinder test to assess the accuracy of Method 6.

In terms of experimental design, the Cambridge test of Method 6 was similar in nearly all aspects to the Dayton test. Only a few of the details were different. The four Cambridge blocks had SO_2 concentration levels around 145 X 10^{-7}, 550 X 10^{-7}, 830 X 10^{-7}, and 1010 X 10^{-7} lb/scf. The time interval between runs within a block was reduced from 60 min on the Dayton test to 45 min on the Cambridge test as the collaborators became more proficient in sampling set-up. The intent was to minimize drift in the true emission concentration during each block's runs by conducting these runs in the shortest feasible time frame.

*EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will result in undue cost or difficulty in clarity, NERC/RTP is providing conversion factors for the particular nonmetric units used in the document. For this report, the factor is:

$$10^{-7} \text{ lb/scf} = 1.6017 \times 10^{-3} \text{ } \mu\text{g/m}\ell$$

Various potential complications result from the real-world conduct of a mathematically idealized experimental design because the ideal assumptions on which a straight forward statistical analysis of the experimental design is based may prove to be wholly or partially invalid in the actual practical application. In the randomized block designs for the Method 6 tests conducted at Dayton and Cambridge, there are two readily apparent possible complications. The first is that the true SO_2 emission concentration in the stack, instead of remaining constant throughout the four runs comprising a block as the randomized block design implies, does in fact vary significantly during the block's runs. Should such "true drift" actually occur within a four-run block, it would invalidate the usual repeatability determination technique. It should be noted that because the time intervals between the runs within a block were necessarily larger on the Method 6 tests (45 to 60 min) than on the Method 7 tests (15 to 25 min), the existence of the true drift situation is more likely in the Method 6 collaborative test data. The second potential complication is the existence of a port effect. Although the four ports through which the collaborative teams simultaneously sample were designed so as to be geometrically equivalent, they do not, of course, provide all four teams with access to the same sampling location at the same time. Thus, there is a possibility that there are consistent differences between the true SO_2 concentrations at the sampling ports, some having consistently higher SO_2 concentrations than others. If this phenomenon exists, it is termed a port effect. If either of these potential complications exist to the extent that they are detectable in the collaborative test data, then suitable statistical techniques must be applied to counteract such effects by appropriately adjusting the reported test data prior to statistical analysis.

In addition to the Method 6 collaborative test itself, two auxiliary tests were also conducted at both the Dayton and Cambridge sites to complement the information regarding Method 6 available from the collaborative tests. A gas cylinder accuracy test was conducted to provide a good independent assessment of the accuracy of Method 6. This test involved three different standard gas cylinders furnished by Scott Research Laboratories at each test site that contained mixtures of sulfur dioxide and nitrogen. Scott Research determined the sulfur dioxide concentration of each cylinder with an accuracy of ±1 percent. The three gas cylinders were labeled X, Y, and Z. On each of the four collaborative test days, each collaborative team obtained one sample from each cylinder according to the Method 6 procedure. These samples were later analyzed in the laboratory along with the day's collaborative test samples. Thus, the Method 6 values can be compared against the Scott Research measurements which were unknown to the collaborative teams to determine the accuracy and any possible bias in Method 6.

The second test involved the repeated analytical determination of the SO_2 concentration implicit in four unknown sulfate solutions to isolate the accuracy and precision of the sample analysis phase of Method 6. Four accurately determined sulfuric acid solutions were prepared by Southwest Research Institute and furnished to each collaborative team for sample analysis, together with the collaborative test and gas cylinder samples. A complete factorial design was specified for this unknown sulfate solution test in which each laboratory was to analyze a 10-mℓ aliquot of each solution in triplicate on each of three days during which each site's test samples were being analyzed. An example of the unknown sulfate solution instruction and reporting form is presented as Figure 8.

B. The Collaborative Test Data

In Section B.1 of Appendix B, the original reported Method 6 collaborative test data are presented and a preliminary analysis of this data is conducted. The apparent outlier points were recalculated. Through this process, considerable calculation errors were uncovered in Lab 102's SO_2 concentration values. The presence of these calculation errors suggests the need for a standard EPA computer program for Method 6 to calculate the SO_2 concentration from the raw input to be provided in the

Collaborative Test of Method 6
Instructions for Analysis of Unknown Sulfate Solutions

A series of sulfate solutions are provided to each collaborator. These solutions are labeled A, B, C, and D, and the concentrations are unknown to the collaborators.

Each unknown solution is to be analyzed in triplicate on each of three separate days. Use a 10 ml aliquot and follow the procedure in Section 4.3 of Method 6 and report results as lb/ft^3 assuming a sample volume of 1 cubic foot at standard conditions.

Submit the results on this sheet along with your other collaborative test data.

Analyst _____ Lab 104

		Concentration, lb/ft^3			
Day	Replicate	Solution A	Solution B	Solution C	Solution D
Day 1 Date 3-13-73	1	3.61×10^{-5}	0	5.35×10^{-5}	1.81×10^{-5}
	2	3.63 "	0	5.35 "	1.80 "
	3	3.59 "	0	5.35 "	1.78 "
Day 2 Date 3-14-73	1	3.56 "	0	5.34 "	1.80 "
	2	3.54 "	0	5.36 "	1.81 "
	3	3.56 "	0	5.36 "	1.80 "
Day 3 Date 3-15-73	1	3.59 "	0	5.44 "	1.83 "
	2	3.61 "	0	5.41 "	1.81 "
	3	3.58 "	0	5.32 "	1.83 "

Figure 8. Collaborative Test of Method 6. Instructions for Analysis of Unknown Sulfate Solutions

specified units. The preliminary analysis also uncovered a *potentially serious weakness of Method 6: the repeated collection of extraordinarily low SO_2 samples without any field indication that the sampling had been deficient.* Six of these very low samples were collected (three by Lab 102 at Dayton and three by Lab 101 at Cambridge). Both Labs 101 and 102 felt that malfunctioning of the sampling train, probably a leak that went undetected despite performance of the method's leak testing procedure, was the cause of their low samples. Lab 102 had substantial evidence to support its claim of leakage and its location of this leakage in the socket joint of the midget bubbler that connected to the ball joint off the probe. After Lab 102 accidently broke and replaced the bubbler in one of its two sampling trains, its low SO_2 sampling problem disappeared. Efforts must be made to determine if this sporadic under-sampling problem which apparently afflicts Method 6 is due to leakage or to some other malfunction in the sampling apparatus. Then a means of detecting the problem condition in the field before or during Method 6 sample collection must be devised and suitable acceptance criteria established. The six extraordinarily low sample values were considered erroneous because of probable sampling train malfunction, and thus rejected.

The corrected Method 6 collaborative test data from the Dayton site and from the Cambridge site are presented in Tables 2 and 3, respectively. All observed calculation errors have been corrected in these tables. Also, the one missing observation of Lab 102 and the six erroneous observations of Labs 101 and 102 were given replacement values according to the minimum variance unbiased estimating procedure described in Section B.4 of Appendix B under the variance stabilizing logarithmic transformation. Tables 2 and 3 also provide run, collaborator, and port summaries consisting of the mean, the standard deviation, and, for each run, the coefficient of variation.

Two possible complications to the statistical analysis, because of the idealized assumptions usually made in this analysis, are examined in Appendix B. These complications were described in the previous section. The possibility that a significant port effect was present in the corrected collaborative test data gathered at either the Dayton or the Cambridge site is explored in Section B.2 of Appendix B. No significant port effect is detectable in either site's data. The other complication, that the true SO_2 concentration may have drifted substantially from run to run within some blocks of the collaborative test data, is investigated in Section B.3 of Appendix B. By comparing the within-laboratory and the between-laboratory coefficient of variation estimates for each block, it is discovered that the within-laboratory estimates are larger than the expected maximum in five of the eight blocks. Drift in the true SO_2 concentration is a plausible explanation for this. Furthermore, in three of these five blocks, there is a significant positive correlation over the block's four runs between the average of the collaborators Method 6 values and the site's best SO_2 monitoring method. A significant positive correlation indicates that both the Method 6 averages and the monitoring method readings rise and fall simultaneously. The only reasonable explanation for such synchronous Method 6 and monitoring SO_2 measurements in these three blocks is that corresponding variations in the true SO_2 concentration have caused them. It is therefore concluded that *these three blocks, the third and fourth blocks of Dayton data and the second block of Cambridge data, were subject to substantial drift in the true SO_2 concentration from run to run.* However, in the other two blocks with excessive within-laboratory variation, there is insufficient evidence to warrant this conclusion as the explanation. The corrected collaborative test data in the three drifted blocks were adjusted for the drift so that reasonable within-laboratory standard deviation and repeatability estimates could be made. The adjustment used gave the same Method 6 mean to each run in an adjusted block. The adjusted Method 6 collaborative test data are shown in Tables B-7 and B-8 (Appendix B) with the adjusted points denoted with a "†" symbol. As a result of adjustment, the within-laboratory coefficient of variation estimates assume reasonable values.

Table 2. The Corrected Dayton Collaborative Test Data With Replacement Values

METHOD: METHOD 6 --- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CORRECTED SO2 CONC. AT STD. COND. WITH REPLACEMENTS (DRY BASIS), 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: DAYTON

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104

INTER-LABORATORY RUN SUMMARY

		LAB 101		LAB 102		LAB 103		LAB 104		RUN SUMMARY		
RUN	SAMPLE	DATA	PORT	DATA	PORT	DATA	PORT	DATA	PORT	MEAN	STD DEV	COEF OF VAR
1	1	724.	(B)	998.	(C)	903.	(A)	719.	(D)	823.5	119.9	.1999
2	2	912.	(C)	929.*	(D)	919.	(B)	736.	(A)	871.5	90.5	.1038
3	3	789.	(D)	819.	(A)	828.	(C)	763.	(B)	798.5	28.6	.0359
4	4	865.	(A)	910.*	(B)	860.	(D)	786.	(C)	855.2	51.9	.0600
5	11	595.	(C)	602.*	(D)	600.	(B)	558.	(A)	588.7	20.7	.0352
6	12	612.	(D)	589.	(A)	572.	(C)	526.	(B)	573.5	35.8	.0625
7	13	586.	(A)	583.*	(B)	582.	(D)	528.	(C)	569.7	27.9	.0489
8	14	588.	(B)	607.	(C)	599.	(A)	539.	(D)	582.0	32.4	.0566
9	15	175.	(D)	203.	(A)	183.	(C)	172.	(B)	183.2	14.0	.0762
10	16	182.	(A)	180.	(B)	185.	(D)	184.	(C)	182.7	2.2	.0121
11	17	170.	(B)	182.	(C)	180.	(A)	169.	(D)	175.2	6.7	.0382
12	18	157.	(C)	174.	(D)	168.	(B)	166.	(A)	166.2	7.0	.0424
13	25	1040.	(A)	1070.	(B)	1037.	(D)	889.	(C)	1009.0	81.4	.0806
14	26	1060.	(B)	1202.	(C)	1142.	(A)	986.	(D)	1097.5	99.9	.0860
15	27	1170.	(C)	1209.	(D)	1176.	(B)	1089.	(A)	1161.0	51.0	.0439
16	28	1090.	(D)	1084.	(A)	1147.	(C)	1009.	(B)	1082.5	56.6	.0523

COLLABORATOR SUMMARY

COLLABORATOR	LAB 101	LAB 102	LAB 103	LAB 104
MEAN	670.0	709.7	692.2	613.1
STD. DEVIATION	351.1	371.6	365.1	313.7

PORT SUMMARY

PORT	A	B	C	D
MEAN	670.7	663.4	680.6	665.1
STD. DEVIATION	347.0	350.9	349.7	349.2

*Replacement value.

Table 3. The Corrected Cambridge Collaborative Test Data With Replacement Values

METHOD: METHOD 6 --- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CORRECTED SO2 CONC. AT STD. COND. WITH REPLACEMENTS (DRY BASIS), 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: CAMBRIDGE

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104

INTER-LABORATORY RUN SUMMARY

RUN	SAMPLE	LAB 101 DATA	LAB 101 PORT	LAB 102 DATA	LAB 102 PORT	LAB 103 DATA	LAB 103 PORT	LAB 104 DATA	LAB 104 PORT	RUN SUMMARY MEAN	RUN SUMMARY STD DEV	RUN SUMMARY COEF OF VAR
1	4	139.	(D)	153.	(B)	156.	(C)	150.	(A)	144.2	7.1	.0478
2	5	142.*	(A)	146.	(C)	143.	(D)	147.	(B)	144.5	2.4	.0165
3	6	152.	(B)	146.	(D)	151.	(A)	143.	(C)	148.0	4.2	.0287
4	7	143.*	(C)	143.	(A)	150.	(B)	147.	(D)	145.7	3.4	.0234
5	8	412.	(A)	513.	(C)	484.	(D)	502.	(B)	479.0	45.7	.0455
6	9	547.	(B)	568.	(D)	516.	(A)	522.	(C)	550.7	38.6	.0701
7	10	565.	(C)	604.	(A)	556.	(B)	560.	(D)	572.5	24.6	.0430
8	11	543.	(D)	624.	(B)	544.	(C)	604.	(A)	543.8	33.4	.0563
9	18	847.	(B)	826.	(D)	844.	(A)	805.	(C)	830.5	19.4	.0233
10	19	807.	(C)	838.	(A)	812.	(B)	809.	(D)	816.5	14.5	.0177
11	20	837.	(D)	824.	(B)	787.	(C)	834.	(A)	820.5	23.0	.0280
12	21	862.	(A)	850.	(C)	838.	(D)	825.	(B)	843.8	15.4	.0188
13	24	990.	(C)	1123.	(A)	1061.	(B)	1007.	(D)	1032.7	77.4	.0754
14	26	990.	(D)	882.	(B)	1061.	(C)	961.	(A)	973.5	79.1	.0761
15	27	1020.*	(A)	1086.	(C)	1053.	(D)	997.	(B)	1039.0	38.4	.0374
16	28	990.	(B)	899.	(D)	1070.	(A)	999.	(C)	984.5	70.1	.0709

COLLABORATOR SUMMARY

COLLABORATOR	LAB 101	LAB 102	LAB 103	LAB 104
MEAN	627.2	639.7	639.7	625.7
STD. DEVIATION	334.8	337.1	351.8	329.4

PORT SUMMARY

PORT	A	B	C	D
MEAN	492.4	632.7	629.4	627.7
STD. DEVIATION	353.8	327.8	334.7	332.2

*Replacement value.

C. The Accuracy of Method 6

One of the major tasks of this collaborative study is to determine if Method 6 gives accurate (i.e., unbiased) measurements of the true SO_2 concentration emitted by the stationary source being sampled. As discussed in *The Experimental Design* section, the gas cylinder test was designed as the primary means to ascertain the accuracy of Method 6. At each test site, three different standard gas cylinders, obtained from Scott Research Laboratories and containing known mixtures of sulfur dioxide and nitrogen, served as the SO_2 source for Method 6 sampling. Samples were collected by each collaborator from each cylinder on each of the four test days. The corrected Method 6 SO_2 concentrations obtained are presented and summarized in Tables 4 and 5, respectively, for the Dayton and Cambridge cylinder data. Three erroneous measurements were obtained by Lab 102 from Cylinder Z at the Dayton site, apparently due to that sporadic leakage problem discussed previously. These erroneous Lab 102 measurements are denoted in Table 4 by an E following their value; they were not included in the calculation of any of the summary statistics shown in this table.

A summary of the pertinent accuracy data on Method 6 from the gas cylinder test is presented in Table 6. For each cylinder at the two test sites, Table 6 displays the "true value" determined by Scott Research for the cylinder, the mean of the collaborators' Method 6 measurements from the cylinder, uncertainty intervals for both these values, and the percentage difference in their values. The 95-percent confidence interval for the collaborators' Method 6 mean is based on a variance of $\hat{\sigma}_L^2/4 + \hat{\sigma}^2/12$, where $\hat{\sigma}_L^2$ and $\hat{\sigma}^2$ are the variance estimates derived in Section B.5 (Appendix B) for Method 6. The Table 6 accuracy values and intervals are plotted in Figure 9. The only Method 6 95-percent confidence intervals that include the Scott Research determinations are for the two low concentration cylinders, cylinder Y at Dayton and cylinder X at Cambridge. The obvious inference to be drawn from Table 6 and Figure 9 is that *Method 6 is unbiased at low concentrations, but at concentrations above* 500×10^{-7} *lb/scf, Method 6 acquires a low value bias with a magnitude of about 5 to 10 percent of the reported value.*

A potential means of verifying this Method 6 accuracy conclusion is through the Envirometrics SO_2 monitor readings for the Dayton test and through the Walden calculated SO_2 values and Dynasciences SO_2 monitor readings for the Cambridge test. The data for these three alternative accuracy measures on each run are contained in Table B-6. However, examination of Table B-6 reveals enough inconsistencies among these three alternative measures when compared against the Method 6 run mean to rule out their use as an accuracy determination basis. Thus, the gas cylinder test is the only valid means of determining the accuracy of Method 6 available in this study. In conclusion, Method 6 is unbiased at low SO_2 concentrations, but acquires a 5- to 10-percent low value bias at higher concentrations.

D. The Precision of Method 6

Various aspects of the precision of Method 6 are estimable from the Method 6 collaborative tests conducted at Dayton and Cambridge. The variance component standard deviations gauge the variability in a single Method 6 SO_2 concentration determination c relative to other determinations. The *within-laboratory standard deviation* σ measures the variability relative to other determinations by the *same laboratory* using the same field operators, laboratory analyst, and equipment at the same true SO_2 concentration level μ. The *laboratory bias standard deviation* σ_l measures the amount of variability in Method 6 determinations due to changes in the field operators, the analysts, the instrumentation and the unspecified Method 6 procedural details employed by *different laboratories* or by the *same laboratory at different times.* The *between-laboratory standard deviation* σ_b measures the total variation in simultaneous Method 6 determinations by different laboratories at the same true SO_2 concentration μ:

Table 4 The Dayton Gas Cylinder Test Data

METHOD: METHOD 6 --- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CORRECTED SO2 CONC. AT STD. COND. FROM GAS CYLINDERS, DRY BASIS, 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: DAYTON

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104

INTER-LABORATORY RUN SUMMARY

RUN	SAMPLE	LAB 101 DATA	LAB 101 PORT	LAB 102 DATA	LAB 102 PORT	LAB 103 DATA	LAB 103 PORT	LAB 104 DATA	LAB 104 PORT	RUN SUMMARY MEAN	RUN SUMMARY STD DEV	RUN SUMMARY COEF OF VAR
1	7	129.	(Y)	140.	(Y)	137.	(Y)	134.	(Y)	136.2	5.0	.0366
2	8	130.	(Y)	143.	(Y)	132.	(Y)	132.	(Y)	134.2	5.4	.0400
3	20	120.	(Y)	136.	(Y)	124.	(Y)	123.	(Y)	127.0	7.1	.0557
4	24	122.	(Y)	134.	(Y)	128.	(Y)	114.	(Y)	126.2	7.5	.0594
5	6	625.	(Z)	44. E	(Z)	630.	(Z)	594.	(Z)	609.7	31.8	.0508
6	9	631.	(Z)	64. E	(Z)	641.	(Z)	585.	(Z)	619.0	29.4	.0482
7	21	611.	(Z)	265. E	(Z)	607.	(Z)	572.	(Z)	596.7	21.5	.0360
8	22	612.	(Z)	658.	(Z)	640.	(Z)	567.	(Z)	619.2	39.6	.0640
9	5	1110.	(X)	1349.	(X)	1260.	(X)	1123.	(X)	1209.2	112.4	.0931
10	10	1260.	(X)	1277.	(X)	1279.	(X)	1163.	(X)	1244.7	55.2	.0443
11	19	1270.	(X)	1294.	(X)	1292.	(X)	1138.	(X)	1236.0	68.7	.0556
12	23	1260.	(X)	1320.	(X)	1256.	(X)	1071.	(X)	1226.7	107.9	.0879

COLLABORATOR SUMMARY

COLLABORATOR	LAB 101	LAB 102	LAB 103	LAB 104
MEAN	656.7	716.9	673.9	608.8
STD. DEVIATION	471.5	585.7	482.1	425.8

PORT SUMMARY

PORT	X	Y	Z
MEAN	1229.2	130.9	611.8
STD. DEVIATION	81.2	7.3	29.5

E Erroneous measurement excluded from the calculations.

Table 5. The Cambridge Gas Cylinder Test Data

METHOD: METHOD 6 --- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CORRECTED SO2 CONC. AT STD. COND. FROM GAS CYLINDERS, DRY BASIS, 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: CAMBRIDGE

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104

INTER-LABORATORY RUN SUMMARY

RUN	SAMPLE	LAB 101 DATA	LAB 101 PORT	LAB 102 DATA	LAB 102 PORT	LAB 103 DATA	LAB 103 PORT	LAB 104 DATA	LAB 104 PORT	RUN SUMMARY MEAN	RUN SUMMARY STD DEV	RUN SUMMARY COEF OF VAR
1	3	199.	(X)	197.	(X)	159.	(X)	193.	(X)	197.0	5.0	.0338
2	12	138.	(X)	193.	(X)	192.	(X)	153.	(X)	194.0	6.9	.0443
3	16	191.	(X)	196.	(X)	199.	(X)	157.	(X)	198.2	6.7	.0452
4	23	191.	(X)	130.	(X)	196.	(X)	153.	(X)	192.5	9.7	.0479
5	2	595.	(Z)	670.	(Z)	651.	(Z)	605.	(Z)	625.2	93.2	.0691
6	14	699.	(Z)	608.	(Z)	693.	(Z)	631.	(Z)	631.5	16.7	.0265
7	15	535.	(Z)	896.	(Z)	697.	(Z)	556.	(Z)	686.0	191.9	.2197
8	24	696.	(Z)	637.	(Z)	653.	(Z)	638.	(Z)	693.5	7.5	.0117
9	1	1290.	(Y)	1309.	(Y)	1157.	(Y)	1261.	(Y)	1253.0	66.5	.0530
10	13	1270.	(Y)	1296.	(Y)	1230.	(Y)	1298.	(Y)	1260.5	27.7	.0220
11	17	1290.	(Y)	1253.	(Y)	1228.	(Y)	1083.	(Y)	1213.5	90.7	.0747
12	22	1300.	(Y)	1320.	(Y)	1215.	(Y)	1238.	(Y)	1264.2	49.8	.0393

COLLABORATOR SUMMARY

COLLABORATOR	LAB 101	LAB 102	LAB 103	LAB 104
MEAN	676.2	708.2	667.9	655.5
STD. DEVIATION	493.0	496.5	452.5	459.2

PORT SUMMARY

PORT	X	Y	Z
MEAN	195.9	1298.8	634.4
STD. DEVIATION	6.8	60.9	67.9

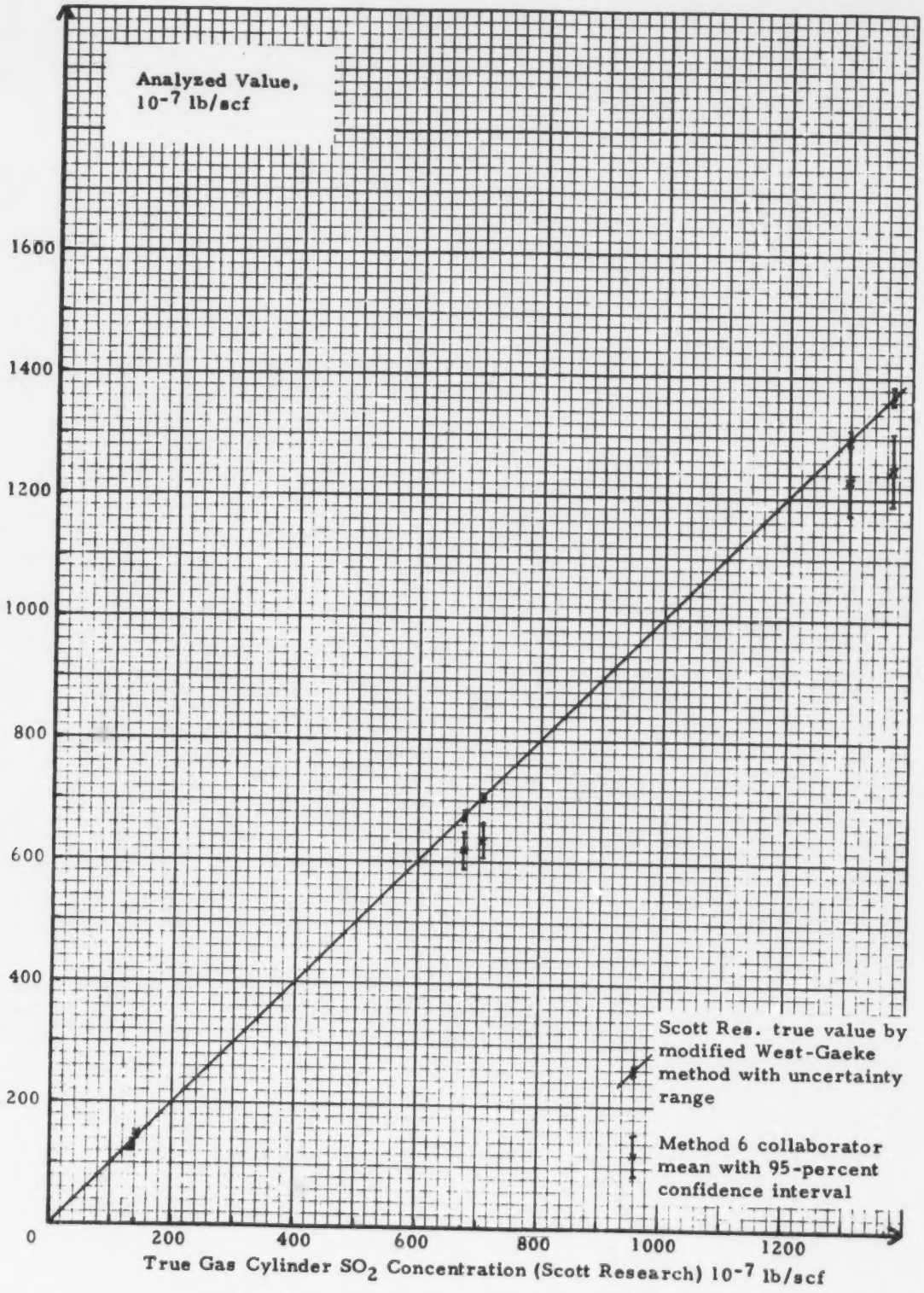

Figure 9. Method 6 Accuracy From Standard Gas Cylinder Data

Table 6. Method 6 Accuracy From SO_2 Standard Gas Cylinder Test

Test Site	Cylinder	Sulfur Dioxide Concentration, 10^{-7} lb/scf				Mean Percentage Difference, %
		True Value–Scott Research*		Method 6		
		Value	±1-Percent Uncertainty Range	Collab. Mean	95-Percent Confidence Interval for Mean	
Dayton	Y Low	137.0	(135.6, 138.4)	130.9	(124.7, 137.1)	−4.5
	Z Medium	676	(669,683)	620.4	(589.7, 651.2)	−8.2
	X High	1300	(1287, 1313)	1229.2	(1170.5, 1287.9)	−5.4
Cambridge	X Low	142.8	(141.4, 144.2)	145.4	(138.5, 152.3)	+1.8
	Z Medium	706	(699,713)	636.6	(606.2, 667.0)	−9.8
	Y High	1370	(1356, 1384)	1248.8	(1189.2, 1308.4)	−8.8

*Scott Research measured the SO_2 concentration of each cylinder by a modification of the West-Gaeke method in which the cylinder sample was diluted in glass to about 3 ppm prior to the West-Gaeke determination.

it is a composite of σ and σ_L: $\sigma_b^2 = \sigma^2 + \sigma_L^2$. Other useful precision measures, the repeatability and reproducibility standard deviations, are derived from the component standard deviation measures to provide similar information regarding a Method 6 test result. Throughout this report, *the value t of a Method 6 test result T is defined as the average of three Method 6 repetitions, where each repetition is the average of two Method 6 SO_2 concentration determinations* c_{ri} sampled at 1-hr intervals:

$$t = \frac{1}{3}\sum_{r=1}^{3}\left(\frac{1}{2}\sum_{i=1}^{2} c_{ri}\right) = \frac{1}{6}\sum_{1}^{6} c_{ri}$$

This test result definition is admittedly somewhat deficient and artificial. Each repetition of a Method 6 performance test for compliance at fossil fuel-fired steam generator plants is stipulated in the *Federal Register*[2] as the determined SO_2 emissions rate $Q_s\,\bar{c}_r$. Here Q_s is the volumetric flow rate determined experimentally by Method 2 in conjunction with Methods 1, 3, and 4. The obvious deficiency of T is that the emissions rate $Q_s\,\bar{c}_r$, rather than the average SO_2 concentration $\bar{c}_r = \frac{1}{2}\sum_{i=1}^{2} c_{ri}$, defines a repetition. T is artificial because it is not actually the criterion to be used in compliance performance testing. But the actual SO_2 criterion, the emissions rate averaged over three repetitions, requires concurrent precision analyses of Methods 1, 2, 3, and 4 in addition to Method 6. Hence it is beyond the scope and intent of this report, which pertains exclusively to Method 6. However, T is extremely useful for determining the precision characteristics of Method 6 in the compliance performance testing framework. Except for the volumetric flow rate factor, T does reflect the compliance performance test situation in which Method 6 will be used—three repetitions each consisting of two SO_2 samples taken according to Method 6.[3] Thus, T accurately represents the Method 6 contribution to the average SO_2 emissions rate criterion used in compliance performance testing. Consequently, the repeatability and reproducibility standard deviations, $\sigma/\sqrt{m}$ and $\sqrt{\sigma_L^2 + \sigma^2/m}$, respectively, for Method 6 are appropriately specified with respect to the test result T, so that $m = 6$.

The precision estimates for Method 6 were obtained by a coefficient of variation analysis. The fundamental assumption of this analysis, that the Method 6 variance component standard deviations are actually proportional to the true SO_2 concentration sampled, is examined in Section B.4 of

Appendix B on the collaborative test data. Analysis of this data reveals that both the within-laboratory standard deviation σ and the between-laboratory standard deviation σ_b of Method 6 can be considered proportional to the true SO_2 concentration μ. These conclusions from Section B.4 of Appendix B are based on plots and regressions of the appropriate data, and on the implications of the finding that the logarithmic data transformation best achieves equality of run variance. It was demonstrated in the prior Method 7 collaborative test report[4] that the proportionality of both σ and σ_b to μ implies that the laboratory bias component standard deviation σ_L is also proportional to μ. Hence the proportionality prerequisite to using the coefficient of variation analysis in estimating the precision measures of Method 6 is satisfied.

All the standard precision measures of Method 6 are calculated in Section B.5 of Appendix B, both from the Dayton and Cambridge Collaborative test data itself and from the gas cylinder test data from these sites. The coefficient of variation analysis is the basis for these calculations. The precision estimates obtained are summarized in Table 7. Here c is the value of a Method 6 determination, whereas t is the value of a Method 6 test result. Note that the Method 6 precision estimates from the

Table 7. Method 6 Precision Variability Estimates

Source of Test Data	Precision Variability Measure	Test Data Version	Component Estimates		Test Result Estimates	
			Coef. of Var. $\hat{\beta}$	Std. Dev., $\hat{\sigma}$	Std. Dev.	Mandel Def.
Collaborative Test	Within Lab	ADJ	$\hat{\beta} = 0.040$	$\hat{\sigma} = 0.040\ c$		
	Between Labs	CWR	$\hat{\beta}_b = 0.058$	$\hat{\sigma}_b = 0.058\ c$		
	Lab Bias	Comp.	$\hat{\beta}_L = 0.042$	$\hat{\sigma}_L = 0.042\ c$		
	Repeatability (m = 6)	ADJ			0.016 t	0.045 t
	Reproducibility (m = 6)	Comp.			0.045 t	0.125 t
Gas Cylinder Test	Within Lab	CD	$\hat{\beta} = 0.044$	$\hat{\sigma} = 0.044\ c$		
	Between Labs	CD	$\hat{\beta}_b = 0.063$	$\hat{\sigma}_b = 0.063\ c$		
	Lab Bias	CD	$\hat{\beta}_L = 0.044$	$\hat{\sigma}_L = 0.044\ c$		
	Repeatability (m = 6)	CD			0.018 t	0.050 t
	Reproducibility (m = 6)	CD			0.048 t	0.132 t

*Test Data Version Codes:
CD — Corrected data.
CWR — Corrected data with replacement values.
ADJ — Corrected data with replacements adjusted for true drift.
Comp. — Composite of CWR and ADJ data set estimates.

collaborative test data are derived from different versions of the data. The between-laboratory standard deviation estimate $\hat{\sigma}_b$ is made from the corrected collaborative test data with replacement values shown in Tables 2 and 3. This is the valid version of the test data because the between-laboratory variability on each run is not affected by the drift in the true SO_2 concentration that was discovered in Section B.3 of Appendix B. However, this drift does interfere with the within-laboratory variability estimation which involves comparing a laboratory's Method 6 SO_2 determinations over the four runs in a block. Hence, the σ and repeatability estimates for Method 6 are derived from the corrected collaborative test data with replacements adjusted for true drift, which is displayed in Tables B-7 and B-8. Since $\sigma_L^2 = \sigma_b^2 \quad \sigma^2$, the laboratory bias standard deviation estimate is a composite derived from both of these collaborative test data sets. Similarly, the reproducibility estimate is also a composite. By contrast, all the

Method 6 precision estimates from the gas cylinder test are obtained from the same data set, i.e., the corrected gas cylinder data presented in Tables 4 and 5. The agreement between the collaborative test data and the gas cylinder test data in the derived Method 6 precision estimates is excellent. Not only are the comparable estimates of similar magnitude, but the proportions of the between-laboratory variance attributable to the within-laboratory and the laboratory bias components remain remarkably constant. The uncertainty in the Method 6 test result reproducibility and repeatability estimates due to the design limitations of the collaborative test are also investigated in Section B.5 of Appendix B. With a 7.2 percent percentage uncertainty, the 95-percent confidence interval about the Method 6 repeatability standard deviation estimate, 1.6 percent of the test result value t, is from 1.4 to 1.9 percent of t. The estimated *reproducibility standard deviation* of a Method 6 test result, *4.5 percent of t*, has a much larger percentage uncertainty of 36.5 percent because the collaborative test had to be restricted to only four collaborators. Consequently, the 95-percent confidence interval for the true reproducibility standard deviation of a Method 6 test result is much broader, ranging from 1.3 to 7.7 percent of t. *Mandel[5] defines repeatability and reproducibility as the quantities that would be exceeded only 5 percent of the time by the difference between two randomly selected test results: for repeatability both test results are obtained by the same laboratory; for reproducibility, the test results come from different laboratories.* Using Mandel's definition, the repeatability of a Method 6 test result is 4.5 percent of its value and its reproducibility is 12.5 percent of its value.

E. Accuracy and Precision of the Analytical Phase

An unknown sulfate solution test was conducted along with the Method 6 collaborative study to assess the accuracy and precision of the analytical phase of Method 6 separately. Four different sulfate solutions, with the actual concentrations concealed, were provided each collaborative laboratory for Method 6 sample analysis, along with the collaborative test and gas cylinder samples. Sample aliquots of 10 mℓ each from each solution were to be analyzed by every collaborative team in triplicate on each of three sample analysis days along with the samples from both test sites. The reported sulfate solution data are presented and summarized in Tables B-12, B-13, and B-14 of Appendix B.

The accuracy of the analytical phase of Method 6 can be determined by comparing the average of all the reported Method 6 SO_2 concentrations for each solution against the "true" effective SO_2 concentration represented by that sulfuric acid solution. This comparison is provided in Table 8. The

Table 8. Accuracy of the Analytical Phase of Method 6

Solution	Sulfur Dioxide Concentration, 10^{-7} lb/scf				Percentage Difference, %
	Prepared "True" Value	Collab. Mean	95-Percent Confidence Interval for Mean	Difference	
B	0.00	0.10	(−0.39, 0.59)	+0.10	
D	176.25	174.40	(170.60, 178.20)	−1.85	−1.05
A	352.50	348.97	(341.37, 356.57)	−3.53	−1.00
C	528.75	522.03	(510.63, 533.43)	−6.72	−1.27

95-percent confidence interval for the means over all four collaborators of Solutions D, A, and C is based on a standard deviation of $\sqrt{\hat{\sigma}_L^2/4 + \hat{\sigma}^2/72} = \sqrt{(0.022\mu)^2/4 + (0.011\mu)^2/72} = 0.011\mu$. For the blank Solution B, its actual standard deviation components from Table B-17 are used to compute its interval standard deviation of 0.250. The prepared "true" SO_2 concentration level of each solution lies well within the 95-percent confidence interval about the collaborators' mean Method 6 determination. Thus, *the analytical phase of Method 6 is unbiased within the precision of the method.* The low value bias of Method 6 is not due to its analytical phase.

A separate analysis of variance has been performed on the data for each unknown sulfate solution. These analyses point up a considerable collaborative laboratory site interaction effect and a lesser day

effect as the principal components of the laboratory bias in the Method 6 analytical phase. The laboratory site interaction effect is shown in Section B.6 of Appendix B to be caused partially by variations in the ways different chemists perform the analytical phase of Method 6 and partially by variations that the same chemist introduces into his Method 6 analytical procedure at different times. The inference is that considerable gains in the precision of Method 6 could be made if the analytical procedures were specified in greater detail.

Separate precision estimates for just the analytical phase of Method 6 can be derived from the unknown sulfate solution data. These estimates are obtained in Section B.6 of Appendix B and shown in Table B-18 of the same appendix.

The *minimum detectable limit* for a Method 6 test result is estimated in Section B.7 of Appendix B as 2.1×10^{-7} lb/scf. This value is a conservative estimate: it may well be too large. It represents the smallest Method 6 test result value t that is significantly larger than a zero sulfur dioxide emission concentration when the reproducibility precision of Method 6 is taken into account. Thus, if a laboratory obtains a Method 6 test result that is less than 2.1×10^{-7} lb/scf in performance testing for compliance, such a test result cannot be distinguished from a zero sulfur dioxide emission concentration in the stack.

F. The Sources of Variability in Method 6

The preceding statistical analysis sections provide the basis for analyzing the sources of precision variability in a Method 6 test result. The variability in a test result is measured by its reproducibility variance $\sigma_L^2 + \sigma^2/6$. This formula permits a simple yet informative partitioning of the reproducibility variance into the repeatability variance component $\sigma^2/6$ and the laboratory bias component σ_L^2. Table 9 indicates that this partition apportions 13.2 percent of the Method 6 reproducibility variation to repeatability and the remaining 86.8 percent to laboratory bias. The repeatability component reflects the reduction in the within-laboratory variation in a single Method 6 determination caused by taking duplicate Method 6 determinations on each of three repetitions during performance testing. *The relatively small size of the repeatability component suggests that taking m = 6 replicate Method 6 determinations per performance test is sufficient.* The laboratory bias component reflects all the differences between the laboratories performing the Method 6 collaborative test. These differences include different analysts, different field operators, variation in Method 6 procedural details not specified in the method, measuring instrument variation, etc. Clearly, *the laboratory bias factors are the primary contributors to Method 6 reproducibility variation.* Obviously some laboratory bias factors are unavoidable sources of variation. Others, however, are amenable to improvement.

The reproducibility variance of a Method 6 test result can also be partitioned according to the physical activity and associated location, field sampling or laboratory analysis, that introduces the variability. The unknown sulfate solution test provides an independent assessment of the variability in the laboratory analytical phase of Method 6. The balance of the Method 6 reproducibility variability must be due to field sampling. Table 10 is constructed on this rationale, with the analytical phase variability estimates obtained from Table B-18. Table 10 discloses that only 24.6 percent of the Method 6 reproducibility variation is due to the analytical procedure. *The preponderant 75.4 percent is attributable to field sampling variation sources.* With respect to repeatability variation, the field sampling phase is an even more pronounced source of variation because 92.4 percent of repeatability variation is ascribed to it. In relative terms, the variability caused by the analytical phase of Method 6 is concentrated in the laboratory bias sources where it makes up 27.2 percent of the total. Table 10 makes it clear that the field sampling phase of Method 6 causes much more variation than does the analytical phase. Consequently, if Method 6 is to be improved, it is in the field sampling phase that the major improvements should be sought.

Table 9. Sources of Reproducibility Variation in a Method 6 Test Result

Source of Variance	Estimated Variance Component	Variation Percentage, %
Repeatability	$\hat{\sigma}^2/6 = (0.040\ t)^2/6 = 0.00027\ t^2$	13.2
Laboratory Bias	$\hat{\sigma}^2_L = (0.042\ t)^2 = 0.00176\ t^2$	86.8
Reproducibility	$\hat{\sigma}^2_L + \hat{\sigma}^2/6 = 0.00202\ t^2$	100.0

One major field sampling problem has already been identified in the preliminary analysis of the collaborative test data. This problem, which causes sporadic grossly deficient sample collection, is due to leakage or some similar malfunction in the sampling train. Means must be developed, either to prevent the occurrence of this malfunction, or at least to provide positive evidence that it is occurring so that the sample can be discarded. In fact, the statistical analysis of the Method 6 collaborative test data is based on the assumption that such a means will be developed, because the six outlier points afflicted with this problem were replaced prior to the analysis.

Table 10. The Analytical Phase as a Cause of Method 6 Precision Variation

Source of Variance	Precision Variance in Method 6		Percent Analytical, %	Percent Field, %
	Method 6	Analytical Phase		
Repeatability: $\hat{\sigma}^2/6$	$0.00027\ t^2$	$0.00002\ t^2$	7.6	92.4
Laboratory Bias: $\hat{\sigma}^2_L$	$0.00176\ t^2$	$0.00048\ t^2$	27.2	72.8
Reproducibility: $\hat{\sigma}^2_L + \sigma^2/6$	$0.00202\ t^2$	$0.00050\ t^2$	24.6	75.4

Several specific sources of the Method 6 analytical phase variability have also been identified in the statistical analysis. The unknown sulfate solution test has shown that use of different chemists by the same laboratory to analyze Method 6 samples causes considerable variability. And modifying the details of the analytical procedure that are not specified in the method, either uniformly or haphazardly, is known to cause much of the analytical phase variability. This latter source of variability can be reduced by revising the method as written, either to specify how analytical details should be performed, or to caution against error-inducing situations. For instance, evaporation of some of the isopropanol that is contained in the barium perchlorate titrant will increase the effective normality of the titrant and produce a low bias in the Method 6 determinations obtained. *Thus, a note of caution should be appended to Method 6 warning that all isopropanol-containing solutions be kept in capped containers.*

IV. CONCLUSIONS AND RECOMMENDATIONS

The preceding statistical analysis of the Method 6 collaborative study conducted at the Dayton and Cambridge test sites provides a firm foundation for evaluating Method 6—Determination of Sulfur Dioxide Emissions from Stationary Sources. The following conclusions regarding Method 6 have emerged:

(1) **Accuracy**—Method 6 is accurate at low SO_2 concentrations, but it acquires a low value bias at higher concentrations. The unbiased region is below 300 or 400 $\times 10^{-7}$ lb/scf. Above 500 $\times 10^{-7}$ lb/scf, Method 6 SO_2 concentration determinations tend to lie from 5 to 10 percent below the true concentration, which is a significant difference. The bias lies in the field sampling phase of the method, since analysis of the standard sulfate solutions indicate that the analytical phase of the method is unbiased.

(2) **Precision**—All precision standard deviation measures of a Method 6 SO_2 concentration determination are proportional to the determination itself. The estimated standard deviation of the within-laboratory precision variation in Method 6 determinations, $\hat{o}$, is 4.0 percent of the determination. The estimated standard deviation of the biased laboratory-to-laboratory precision variation, $\hat{o}_L$, is 4.2 percent of the determination. In the compliance performance testing framework, a Method 6 test result t is pragmatically defined as the average of six Method 6 determinations made by a single laboratory. The estimated *repeatability standard deviation* of a test result is $\hat{o}/\sqrt{6} = 1.6$ *percent of* t. The *reproducibility standard deviation* of a test result is estimated as $\sqrt{\hat{o}_L^2 + \hat{o}/6} = 4.5$ *percent of* t. The 95 percent confidence limits for the true standard deviations range from 1.4 to 1.9 percent of t for repeatability, and from 1.3 to 7.7 percent of t for reproducibility. By Mandel's definitions[6], the repeatability of a Method 6 test result is 4.5 percent of t while the reproducibility of a Method 6 test result is 12.5 percent of t.

(3) **Minimum Detectable Limit**—The estimated minimum detectable limit of Method 6 is 2.1 $\times 10^{-7}$ lb/scf. If a Method 6 test result is less than 2.1 $\times 10^{-7}$ lb/scf, the actual sulfur dioxide emission concentration in the stack is indistinguishable from zero. Since this estimate is based on a conservative assumption, the true minimum detectable limit of Method 6 is probably even lower than this.

(4) **Sources of Reproducibility Variation**—The reproducibility variation in a Method 6 test result can be partitioned into its components in two independent ways. The activity phase partition reveals that *75.4 percent of the reproducibility variation occurs in the field sampling phase*, with *only 24.6 percent arising from the laboratory sampling analysis phase*. The source partition divides the reproducibility variance into the *13.2 percent accounted for by repeatability variation* and the remaining *86.8 percent attributable to laboratory bias variation*. Repeatability variation measures the amount of variation in Method 6 test results obtained by a single laboratory on identical groups of replicate samples using the same field operators, the same laboratory analyst, and the same instrumentation. The low repeatability variation suggests that the specified conduct of two Method 6 determinations on each of three repetitions provides sufficient Method 6 replication. The laboratory bias variation reflects the differences that exist, both within the same laboratory and between different laboratories, in the field operators, the analysts, the equipment, and the performance of unspecified Method 6 procedural details that combine to produce Method 6 determinations. Clearly, the major component of the

Method 6 test result reproducibility variance is laboratory bias variation occurring during field sampling; if Method 6 is to be improved substantially, the major effort will have to be directed toward the variability sources causing this component.

Through their experience in performing Method 6, the collaborative laboratories have developed considerable insight into the method's strengths and weaknesses. Two of these laboratories have offered constructive comments on Method 6 and recommendations for improving it.

Walden Research Corporation reports that Method 6 for SO_2 has some weak areas in the sampling section with a proven analytical section. A major defect in Method 6 involves the pump for the sample train as shown in Appendix A, Figure 6-1. The needle valve should be on the vacuum side of the pump with a pressure relief crossover system on the pump. Without this system, the lifetime of a pump is drastically shortened. A vacuum gauge should be put in the line to show plugging of the probe or other malfunction. Regarding sample collection, there is no visible indication even when the impingers are bubbling that a sample of SO_2 is actually being collected in the impingers, even after leak testing the system. The absorbing solution is neutral hydrogen peroxide initially; after sampling to collect a suitable concentration of SO_2, the hydrogen peroxide should become strongly acidic (approximately pH 1-2). Consequently, a simple test with pH indicating paper at the termination of the sampling period will indicate if SO_2 has been collected. This could be performed in the field while the possibility still exists for securing more samples. A short section on the chemical interferences of the barium ion titration with a note for good lighting to see the endpoint would be useful in the analysis section. Lastly, there is no mention in the analysis section of limits on the spread of the results from analysis of identical aliquots. Walden Research ran duplicate, and sometimes even triplicate, titration analyses of the sample solution; the results occasionally differed by 5 percent or more. It is felt that if the titration of identical aliquots differs by 10 percent or more, then more aliquots should be run and those that differ by 10 percent be discarded. If the 10 percent limits are unreasonable, other limits should be set to prevent averaging of widely varying results.

Monsanto Research Corporation has several recommendations. For ease of field work, the glass wash bottles should be replaced with polyethylene bottles. To aid in sample filling and rinsing, 5- and 15-ml graduations ought to be affixed to the bottoms of the midget bubbler and impingers. Finally, to ensure better rinsing of the impingers and connecting tubes, the contents of the storage container should be diluted to 100 ml, instead of 50 ml, in a volumetric flask. Then, all the quantities used during analysis could be doubled to improve the precision of the analytical phase.

The collaborators' recommendations presented above remedy some of the Method 6 weaknesses pointed out in this report. In particular, if the pH indicating paper suggestion for detecting insufficient sample collection proves to be practical, then it could signal in the field that the recurrent Method 6 gross under sampling problem has occurred, and an additional replacement sample could easily be taken. Some such field indicator procedure must certainly be developed for insertion in Method 6 to alleviate this undetected under-sampling problem.

Several additional recommendations are in order. A standard reporting form and an accompanying computer program should be developed for Method 6. The raw Method 6 measurements would be recorded in specified units on the reporting form, keypunched, and input to the computer program which would calculate the corresponding sulfur dioxide concentration determinations. While Method 6 is not unusually prone to calculation errors, such a data system would circumvent

the ever-present calculation verification problem. During the statistical analysis, it was discovered that evaporation of isopropanol from the barium perchlorate titrant, when it is left standing in an open container, does occur and will bias the resulting Method 6 SO_2 concentration determination. So *a note of caution should be inserted in Method 6 to warn that all solutions containing isopropanol should be kept in capped containers.*

Basically, Method 6 appears to be a reliable SO_2 concentration determination technique. If the current version of Method 6 (cf. Appendix A) is rewritten to specify more of the procedural details, and to incorporate as many of the above recommendations as prove themselves feasible, then it should become a more reliable method for use in field compliance testing at new stationary sources.

APPENDIX A

METHOD 6. DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

Federal Register, Vol. 36, No. 247
December 23, 1971.

PLANT_____

DATE_____

RUN NO._____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			

	VOLUME OF LIQUID WATER COLLECTED		
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g	
FINAL			
INITIAL			
LIQUID COLLECTED			
TOTAL VOLUME COLLECTED		g*	ml

CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER. (1 g. ml):

$$\frac{\text{INCREASE, g}}{(1\ \text{g/ml})} = \text{VOLUME WATER, ml}$$

Figure 5-3. Analytical data.

6.6.2 Concentration in lb./cu. ft.

$$c_s = \frac{\left(\frac{1}{453{,}600}\ \frac{\text{lb.}}{\text{mg.}}\right) M_n}{V_{m_{std}}} = 2.205 \times 10^{-6} \frac{M_n}{V_{m_{std}}} \qquad \text{equation 5-5}$$

where:

c_s = Concentration of particulate matter in stack gas, dry basis, lb./cu. ft. (standard conditions).

453,600 = Mg/lb.

M_n = Total amount of particulate matter collected, mg.

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

6.7 Isokinetic variation.

$$I = \frac{T_s\left[\frac{V_{l_c}(\rho_{H_2O})R}{M_{H_2O}} + \frac{V_m}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{\theta V_s P_s A_n} \times 100$$

$$= \frac{(1.667\ \text{sec./L})(0.0[illegible]\ \text{mm Hg-cu. ft./ml-°R})\left[V_{l_c} + \frac{V_m}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{\theta V_s P_s A_n}$$

Equation 5-6

where:

I = Percent of isokinetic sampling.

V_{l_c} = Total volume of liquid collected in impingers and silica gel (See Fig. 5-3), ml.

ρ_{H_2O} = Density of water, 1 g./ml.

R = Ideal gas constant, 21.83 inches Hg-cu. ft./lb. mole-°R.

M_{H_2O} = Molecular weight of water, 18 lb./lb.-mole.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_m = Absolute average dry gas meter temperature (see Figure 5-2), °R.

P_{bar} = Barometric pressure at sampling site, inches Hg.

ΔH = Average pressure drop across the orifice (see Fig. 5-2), inches H_2O.

T_s = Absolute average stack gas temperature (see Fig. 5-2), °R.

θ = Total sampling time, min.

V_s = Stack gas velocity calculated by Method 2, Equation 2-2, ft./sec.

P_s = Absolute stack gas pressure, inches Hg.

A_n = Cross-sectional area of nozzle, sq. ft.

6.8 Acceptable results. The following range sets the limit on acceptable isokinetic sampling results:

If $90\% \leq I \leq 110\%$, the results are acceptable, otherwise, reject the results and repeat the test.

7. *Reference.*

Addendum to Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, Dec. 6, 1967.

Martin, Robert M., Construction Details of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0581.

Rom, Jerome J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0576.

Smith, W. S., R. T. Shigehara, and W. F. Todd, A Method of Interpreting Stack Sampling Data, Paper presented at the 63d Annual Meeting of the Air Pollution Control Association, St. Louis, Mo., June 14–19, 1970.

Smith, W. S., et al., Stack Gas Sampling Improved and Simplified with New Equipment, APCA paper No. 67-119, 1967.

Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, 1967.

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. A gas sample is extracted from the sampling point in the stack. The acid mist, including sulfur trioxide, is separated from the sulfur dioxide. The sulfur dioxide fraction is measured by the barium-thorin titration method.

1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. *Apparatus.*

2.1 Sampling. See Figure 6-1.

2.1.1 Probe—Pyrex[1] glass, approximately 5 to 6 mm. ID, with a heating system to prevent condensation and a filtering medium to remove particulate matter including sulfuric acid mist.

2.1.2 Midget bubbler—One, with glass wool packed in top to prevent sulfuric acid mist carryover.

2.1.3 Glass wool.

2.1.4 Midget impingers—Three.

2.1.5 Drying tube—Packed with 6 to 16 mesh indicating-type silica gel, or equivalent, to dry the sample.

2.1.6 Valve—Needle valve, or equivalent, to adjust flow rate.

2.1.7 Pump—Leak-free, vacuum type.

2.1.8 Rate meter—Rotameter or equivalent, to measure a 0–10 s.c.f.h. flow range.

2.1.9 Dry gas meter—Sufficiently accurate to measure the sample volu[illegible] within 1%.

2.1.10 Pitot tube—Type S, or equivalent,

[1] Trade names.

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necessary only if a sample traverse is required, or if stack gas velocity varies with time.

2.2 Sample recovery.

2.2.1 Glass wash bottles—Two.

2.2.2 Polyethylene storage bottles—To store impinger samples.

2.3 Analysis.

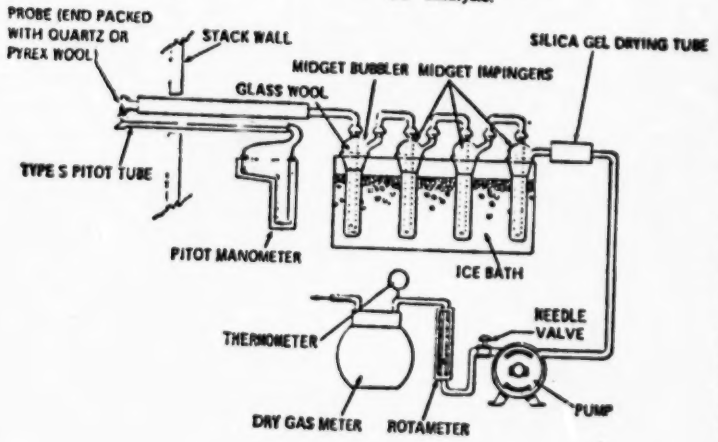

Figure 6-1. SO_2 sampling train.

2.3.1 Pipettes—Transfer type, 5 ml. and 10 ml. sizes (0.1 ml. divisions) and 25 ml. size (0.2 ml. divisions).

2.3.2 Volumetric flasks—50 ml., 100 ml., and 1,000 ml.

2.3.3 Burettes—5 ml. and 50 ml.

2.3.4 Erlenmeyer flask—125 ml.

3. *Reagents.*

3.1 Sampling.

3.1.1 Water—Deionized, distilled.

3.1.2 Isopropanol, 80%—Mix 80 ml. of isopropanol with 20 ml. of distilled water.

3.1.3 Hydrogen peroxide, 3%—dilute 100 ml. of 30% hydrogen peroxide to 1 liter with distilled water. Prepare fresh daily.

3.2 Sample recovery.

3.2.1 Water—Deionized, distilled.

3.2.2 Isopropanol, 80%.

3.3 Analysis.

3.3.1 Water—Deionized, distilled.

3.3.2 Isopropanol.

3.3.3 Thorin indicator—1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt (or equivalent). Dissolve 0.20 g. in 100 ml. distilled water.

3.3.4 Barium perchlorate (0.01 *N*)—Dissolve 1.95 g. of barium perchlorate [$Ba(ClO_4)_2 \cdot 3H_2O$] in 200 ml. distilled water and dilute to 1 liter with isopropanol. Standardize with sulfuric acid. Barium chloride may be used.

3.3.5 Sulfuric acid standard (0.01 *N*)—Purchase or standardize to ±0.0002 *N* against 0.01N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

4. *Procedure.*

4.1 Sampling.

4.1.1 Preparation of collection train. Pour 15 ml. of 80% isopropanol into the midget bubbler and 15 ml. of 3% hydrogen peroxide into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6-1. Leak check the sampling train at the sampling site by plugging the probe inlet and pulling a 10 inches Hg vacuum. A leakage rate not in excess of 1% of the sampling rate is acceptable. Carefully release the probe inlet plug and turn off the pump. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 70° F. or less.

4.1.2 Sample collection. Adjust the sample flow rate proportional to the stack gas velocity. Take readings at least every five minutes and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the tip of the probe at the first sampling point and start the pump. Sample proportionally throughout the run. At the conclusion of each run, turn off the pump and record the final readings. Remove the probe from the stack and disconnect it from the train. Drain the ice bath and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes.

4.2 Sample recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a polyethylene shipment bottle. Rinse the three midget impingers and the connecting tubes with distilled water and add these washings to the same storage container.

4.3 Sample analysis. Transfer the contents of the storage container to a 50 ml. volumetric flask. Dilute to the mark with deionized, distilled water. Pipette a 10 ml. aliquot of this solution into a 125 ml. Erlenmeyer flask. Add 40 ml. of isopropanol and two to four drops of thorin indicator. Titrate to a pink endpoint using 0.01 *N* barium perchlorate. Run a blank with each series of samples.

5. *Calibration.*

5.1 Use standard methods and equipment which have been approved by the Administrator to calibrate the rotameter, pitot tube, dry gas meter, and probe heater.

5.2 Standardize the barium perchlorate against 25 ml. of standard sulfuric acid containing 100 ml. of isopropanol.

6. *Calculations.*

6.1 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (70° F. and 29.92 inches Hg) by using equation 6-1.

$$V_{m_{std}} = V_m \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right) = 17.71 \frac{^\circ R}{\text{in. Hg}} \left(\frac{V_m P_{bar}}{T_m}\right) \quad \text{equation 6-1}$$

where:

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} = Absolute temperature at standard conditions, 530° R.

T_m = Average dry gas meter temperature, °R.

P_{bar} = Barometric pressure at the orifice meter, inches Hg.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.2 Sulfur dioxide concentration.

$$C_{SO_2} = \left(7.05 \times 10^{-4} \frac{\text{lb.-l.}}{\text{g.-ml.}}\right) \frac{(V_t - V_{tb}) N \left(\frac{V_{soln}}{V_a}\right)}{V_{m_{std}}} \quad \text{equation 6-2}$$

where:

C_{SO_2} = Concentration of sulfur dioxide at standard conditions, dry basis, lb./cu. ft.

7.05×10^{-4} = Conversion factor, including the number of grams per gram equivalent of sulfur dioxide (32 g./g.-eq.), 453.6 g./lb., and 1,000 ml./l., lb.-l./g.-ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml.

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

N = Normality of barium perchlorate titrant, g.-eq./l.

V_{soln} = Total solution volume of sulfur dioxide, 50 ml.

V_a = Volume of sample aliquot titrated, ml.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft., see Equation 6-1.

7. *References.*

Atmospheric Emissions from Sulfuric Acid Manufacturing Processes. U.S. DHEW, PHS, Division of Air Pollution, Public Health Service Publication No. 999-AP-13, Cincinnati, Ohio, 1965.

Corbett, P. F. The Determination of SO_x and SO_3 in Flue Gases. Journal of the Institute of Fuel, 34: 237-243, 1961.

Matty, E. E. and E. K. Diehl, Measuring Flue-Gas SO_2 and SO_3. Power *101*: 94-97, November, 1957.

Patton, W. F. and J. A. Brink, Jr., New Equipment and Techniques for Sampling Chemical Process Gases. J. Air Pollution Control Association, *13*, 162 (1963).

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except

APPENDIX B
STATISTICAL METHODS

APPENDIX B. STATISTICAL METHODS

This appendix is composed of various independent sections, each of which contains a statistical analysis pertinent to a particular question or problem encountered in the analysis of the Method 6 collaborative study data. Reference to these sections has been made at various junctures in the Statistical Design and Analysis part of the body of this report.

B.1 Preliminary Analysis of the Original Collaborative Test Data

The original SO_2 collaborative test data from the Method 6 tests conducted at Dayton and Cambridge are shown in Table B-1. The port from which the sample was collected is given in parentheses following the reported SO_2 concentration value. A simplistic outlier analysis was used to detect calculation errors and outlying observations suitable for rejection on physical grounds. A comparison of the four values reported by the collaborators on each run (i.e., for each sample) was made. If either of the extreme values differed from its closest value by more than 10 percent of this value, such outlier observations were extracted for further scrutiny. Each outlier observation was recalculated using the collaborator's reported raw data. Physical grounds for rejection of the outlier observation were sought when it differed greatly from the other three sample values.

Through this process, random and systematic calculation errors and six observations that were low by one or more orders of magnitude were uncovered. All of Lab 102's reported values were high by 9.62 percent of the reported value. This is because Lab 102 obtained a sulfuric acid normality of 0.010869N in its original standardization and used this value in its calculations; a later replicated standardization gave its normality as 0.009915N. Additional Lab 102 calculation errors were also discovered in Samples 12, 14, 15, 16, 17, 18, 25, 26, 27, and 28 at Dayton and in Sample 26 at Cambridge. After these calculation errors had been corrected, there remained six Method 6 observations (Samples 4, 11, and 13 by Lab 102 at Dayton and Samples 5, 7, and 27 by Lab 101 at Cambridge) in which the reported SO_2 concentrations were extraordinarily low. On all six observations, a typical volume of gas had been sampled, but very little barium perchlorate was needed to titrate to a pink endpoint. Lab 102 was utilizing two bubbler-impinger sampling trains alternatively when its low samples were collected. After Sample 13 had been run on February 6, the bubbler in one of these sampling trains was broken in the field. Thereafter, Lab 102's alternate low SO_2 collection problem disappeared. Lab 102 reports that this problem could not be detected in the field despite vigorous leak testing of the sampling train to a no-flow condition on the flowmeter. In their opinion, the malfunction was in the impinger section of the defective sampling train, most likely in the socket joint of the bubbler that connected to the ball joint off the probe. Subsequently, Lab 102 visually inspected all ball-and-socket joints to guard against a recurrence of this problem. Now Lab 101 also felt that one of its two alternated sampling trains did not function properly on its three low-sample runs at Cambridge. It is therefore reasonable to likewise ascribe the three low Lab 101 values at Cambridge to some undetectable leak in one of their sampling trains. On the plausible grounds that a physical malfunction in the sampling train, such as an undetectable leak, had prevented proper Method 6 sampling on all six of the extremely low measurements, these six observations were considered erroneous and treated as if they had been missing observations.

The values of the one missing observation (Dayton, Lab 102, Sample 2) and of the six erroneous observations (Dayton, Lab 102, Samples 4, 11, and 13; Cambridge, Lab 101, Samples 5, 7, and 27) were replaced with suitable correction values. These correction values were the minimum variance unbiased estimates obtained under the variance stabilizing logarithmic transformation

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Table B-1. The Original SO_2 Data From the Method 6 Collaborative Test

Site	Block	Sample	SO_2 Concentration from Method 6, 10^{-7} lb/scf			
			Lab 101	Lab 102*	Lab 103	Lab 104
Dayton	1	1	729 (B)	1040 (C)	903 (A)	714 (D)
		2	912 (C)	Missing (D)	914 (B)	736 (A)
		3	789 (D)	892 (A)	828 (C)	763 (B)
		4	865 (A)	21† (B)	860 (D)	786 (C)
	2	11	595 (C)	38† (D)	600 (B)	558 (A)
		12	612 (D)	672 (A)	572 (C)	526 (B)
		13	586 (A)	46† (B)	582 (D)	528 (C)
		14	588 (B)	697 (C)	599 (A)	534 (D)
	3	15	175 (D)	232 (A)	183 (C)	172 (B)
		16	182 (A)	206 (B)	185 (D)	184 (C)
		17	170 (B)	95 (C)	180 (A)	169 (D)
		18	157 (C)	200 (D)	168 (B)	166 (A)
	4	25	1040 (A)	1234 (B)	1037 (D)	889 (C)
		26	1060 (B)	1382 (C)	1142 (A)	986 (D)
		27	1170 (C)	1385 (D)	1176 (B)	1089 (A)
		28	1090 (D)	1246 (A)	1147 (C)	1009 (B)
Cambridge	1	4	139 (D)	168 (B)	155 (C)	150 (A)
		5	23† (A)	160 (C)	143 (D)	147 (B)
		6	152 (B)	160 (D)	151 (A)	143 (C)
		7	3† (C)	157 (A)	150 (B)	147 (D)
	2	8	412 (A)	562 (C)	489 (D)	502 (B)
		9	597 (B)	623 (D)	516 (A)	522 (C)
		10	565 (C)	668 (A)	556 (B)	560 (D)
		11	593 (D)	690 (B)	549 (C)	604 (A)
	3	18	847 (B)	905 (D)	844 (A)	805 (C)
		19	807 (C)	919 (A)	812 (B)	809 (D)
		20	837 (D)	903 (B)	787 (C)	834 (A)
		21	862 (A)	932 (C)	838 (D)	825 (B)
	4	29	940 (C)	1231 (A)	1061 (B)	1007 (D)
		26	990 (D)	927 (B)	1061 (C)	961 (A)
		27	185† (A)	1190 (C)	1053 (D)	997 (B)
		28	990 (B)	985 (D)	1070 (A)	999 (C)

Note: Port from which sample was collected is shown in parentheses.

*There is a calculation error in these reported values.
†This inordinately low reported value was presumably caused by undetected leaks in the sampling train.

(cf. Section B.4) for the run and block in which they occurred. Table 2 (see main report) contains the corrected Dayton data, and Table 3 of the main report shows the corrected Cambridge data The seven replacement values for the missing and erroneous observations are denoted in these tables by an asterisk following the replacement value.

B.2 Examination of the Port Effect

Because there were just four ports available for sampling at both the Dayton and Cambridge sites, each collaborative team could sample from only one port on each run. Since the possibility of nonuniform flow through the sampling duct always exists, one must determine whether there was a significant sampling port effect in the corrected Method 6 data at either the Dayton or the Cambridge site.

The statistical test used to determine the significance of the port main effect was the rank test that Youden presented in his address, "The Collaborative Test."[7] The application of this rank test to the corrected Method 6 data at both the Dayton and Cambridge sites is shown in Table B-2. Ranks from 1 to 4 were assigned to the ports' data for each run, with a rank of 1 being assigned to the port with the lowest Method 6 value, a rank of 2 to the port with the next higher value, etc. For runs in which one of the collaborators obtained a missing or erroneous data point, a rank of 2.5 was assigned to the port from which this missing or erroneous sample was taken; the other ports were then assigned the ranks 1.25, 2.5, and 3.75 according to their data values. The sixteen ranks assigned to each port on the 16 runs were summed to yield its port rank score. Table B-2 shows that every port rank score is well within the 0.05 lower and upper limits for its two-sided test. Thus, the rank test does not detect any significant port effect in either the Dayton or Cambridge Method 6 test data. However, because of the nature of the randomized block design employed in these tests, a sizable collaborator main effect would tend to obliterate any small port effect that might be present. But since any port effects that might actually have existed have had no detectable influence on the Method 6 test data, the assumption that there are no port effects at either site is valid.

B.3 Data Adjustment for True Drift Within Blocks

For each run of a Method 6 collaborative test, the expected value of the run variance s_j^2 is $E(s_j^2) = \sigma^2 + \sigma_L^2$, where σ^2 is the within-laboratory variance component and σ_L^2 is the laboratory bias variance component. $E(s_j^2)$ is often termed the between-laboratory variance and denoted as σ_b^2. It is demonstrated in Section B.4 that the between-laboratory standard deviation is proportional to the true SO_2 concentration: $\sigma_b = \beta_b \mu$. Thus, $E(s_j^2) = \sigma_b^2 = \beta_b^2 \mu^2$. Since $\sigma_b^2 = \sigma^2 + \sigma_L^2$, one suspects that the within-laboratory standard deviation component σ is also proportional to the concentration mean. This suspicion is strengthened when one recalls that this relationship ($\sigma = \beta\mu$) was true for the Method 7 collaborative tests[8] conducted at these same sites. Hence, let's assume that $\sigma = \beta\mu$ for Method 6 too. The equations $\sigma_b^2 = \sigma^2 + \sigma_L^2$, $\sigma_b = \beta_b \mu$, and $\sigma = \beta\mu$ imply that $\sigma_L = \beta_L \mu$ where β_L is defined by

$$\beta_b^2 = \beta^2 + \beta_L^2$$

Now in most collaborative tests, the within-laboratory variance component estimate $\hat{\sigma}^2$ and the laboratory bias variance component estimate $\hat{\sigma}_L^2$ have the same order of magnitude. Thus, given that $\hat{\sigma}_b^2 = \hat{\beta}_b^2 c^2$ and assuming that $\hat{\sigma}^2 = \hat{\beta}^2 c^2$, where c is the Method 6 SO_2 concentration determination, it is reasonable to expect that the ratio $\hat{\beta}^2/\hat{\beta}_b^2$ will lie between 0.1 and 0.9 for most of the blocks in a collaborative test. Thus, the ratio $\hat{\beta}/\hat{\beta}_b$ will usually lie between 0.3 and 0.95 for most blocks. However, one can expect great variation in the ratio $\hat{\beta}/\hat{\beta}_b$ from block to block, with some values even in excess of 1.0. The $\hat{\beta}_b$ estimate for each run is based on the four collaborators' simultaneous

Table B-2. Youden Rank Test for Significance of Port Effect

Run	Site									
	Dayton					Cambridge				
	Sample	Ranked Data Ports				Sample	Ranked Data Ports			
		A	B	C	D		A	B	C	D
1	1	2	3	1	4	4	3	2	1	4
2	2	3.75	1.25	2.5	2.5	5	2.5	1.25	2.5	3.75
3	3	2	4	1	3	6	2	1	4	3
4	4	1.25	2.5	3.75	2.5	7	3.75	1.25	2.5	2.5
5	11	3.75	1.25	2.5	2.5	8	4	2	1	3
6	12	2	3	4	1	9	4	1	3	2
7	13	1.25	2.5	3.75	2.5	10	1	4	2	3
8	14	2	3	1	4	11	2	1	4	3
9	15	1	4	2	3	18	2	1	4	3
10	16	3	4	2	1	19	1	2	4	3
11	17	2	3	1	4	20	2	3	4	1
12	18	3	2	4	1	21	1	4	2	3
13	25	2	1	4	3	29	1	2	4	3
14	26	2	3	1	4	26	3	4	1	2
15	27	4	2	3	1	27	2.5	3.75	1.25	2.5
16	28	3	4	1	2	28	1	3	2	4
Port Rank Scores:		38.0	43.5	37.5	41.0		35.75	36.25	42.25	45.75
Null Hypothesis:		All sampling ports are equivalent.					All sampling ports are equivalent.			
Alternative Hypothesis:		The true SO_2 concentration sampled differs systematically from port to port.					The true SO_2 concentration sampled differs systematically from port to port.			
Approximate 5 Percent Two-Tailed Limits:		(28.5, 51.5)					(28.4, 51.6)			
Conclusion:		Reject alternative hypothesis. There is no significant port effect.					Reject alternative hypothesis. There is no significant port effect.			

measurements; it contains only three degrees of freedom. Likewise, the experimental design for Method 6 allocated only four measurements by each laboratory in each concentration level block. Hence, the estimate $\hat{\beta}$ also possesses only three degrees of freedom. Thus, each block estimate of $\hat{\beta}/\hat{\beta}_b$ can vary widely from the true underlying ratio β/β_b, but averaging $\hat{\beta}_b$ and $\hat{\beta}$ over many blocks should greatly reduce such variation.

Now let's compare the Method 6 collaborative test data against these expectations. In addition to presenting the corrected Method 6 collaborative test data, Tables 2 and 3 of the main report also provide a run summary (the run mean, standard deviation, and coefficient of variation) on each run at the Dayton and Cambridge sites. The estimate $\hat{\beta}_b$ of the between-laboratory coefficient of variation for a block is computed as the product of the standard deviation unbiasing factor 1.0854 times the average of the four sample coefficients of variation of the block's four runs. Tables B-3 and B-4 present

Table B-3. Within-Laboratory Analysis of Corrected Dayton Collaborative Test Data with Replacements

METHOD: METHOD 6 --- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CORRECTED SO2 CONC. AT STD. COND. WITH REPLACEMENTS (DRY BASIS), 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: DAYTON

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104

INTRA-LABORATORY COLLABORATOR BLOCK SUMMARY

BLOCK	MEAN	COLLABORATOR		MEAN	STD DEV	COEF OF VAR
1	837.2					
		1	LAB 101	823.7	81.0	.0983
		2	LAB 102	899.0	58.8	.0654
		3	LAB 103	876.2	39.7	.0453
		4	LAB 104	749.7	31.9	.0419
2	578.5					
		1	LAB 101	595.2	11.8	.0198
		2	LAB 102	599.0	12.3	.0207
		3	LAB 103	588.2	13.6	.0232
		4	LAB 104	536.5	14.7	.0275
3	176.9					
		1	LAB 101	171.0	10.6	.0617
		2	LAB 102	184.7	12.6	.0684
		3	LAB 103	179.0	7.6	.0425
		4	LAB 104	172.7	7.9	.0457
4	1087.5					
		1	LAB 101	1090.0	57.2	.0524
		2	LAB 102	1141.2	74.5	.0652
		3	LAB 103	1125.5	60.9	.0541
		4	LAB 104	993.2	82.3	.0829

Table B-4. Within-Laboratory Analysis of Corrected Cambridge Collaborative Test Data with Replacements

METHOD: METHOD 6 --- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CORRECTED SO2 CONC. AT STD. COND. WITH REPLACEMENTS (DRY BASIS), 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: CAMBRIDGE

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104

INTRA-LABORATORY COLLABORATOR BLOCK SUMMARY

BLOCK	MEAN	COLLABORATOR		MEAN	STD DEV	COEF OF VAR
1	146.9					
		1	LAB 101	144.0	5.6	.0389
		2	LAB 102	147.0	4.2	.0284
		3	LAB 103	144.7	5.0	.0333
		4	LAB 104	146.7	2.9	.0196
2	549.0					
		1	LAB 101	541.7	87.7	.1618
		2	LAB 102	574.7	51.2	.0884
		3	LAB 103	527.5	31.0	.0588
		4	LAB 104	547.0	45.0	.0822
3	827.8					
		1	LAB 101	838.2	23.2	.0277
		2	LAB 102	834.5	12.0	.0144
		3	LAB 103	820.2	26.2	.0319
		4	LAB 104	818.2	13.6	.0166
4	1008.7					
		1	LAB 101	985.0	33.2	.0337
		2	LAB 102	997.5	124.7	.1250
		3	LAB 103	1061.2	6.9	.0065
		4	LAB 104	991.0	20.5	.0206

the within-laboratory collaborator block summaries for the corrected collaborative test data at Dayton and Cambridge, respectively. The within-laboratory coefficient of variation estimate $\hat{\beta}$ for a block is calculated as 1.0854 times the average of the four collaborators' sample coefficients of variation for that block. A summary of the eight Dayton and Cambridge blocks, including the block estimates $\hat{\beta}_b$, $\hat{\beta}$, and $\hat{\beta}/\hat{\beta}_b$, is shown in Table B-5. This table shows that the ratio $\hat{\beta}/\hat{\beta}_b$ exceeds the usual upper limit of

Table B-5. Block Summary of Within-Laboratory Anomalies

Site	Block	Block Coefficient of Variation Estimates			Run Correlation of Method 6 Means to Monitor Values, r_B	Significance of Run Correlation, $Pr\{r > r_B\}$
		Between Labs, $\hat{\beta}_b$	Within Labs, $\hat{\beta}$	Ratio, $\hat{\beta}/\hat{\beta}_b$		
Dayton	1	0.0935	0.0681	0.73	0.5951	0.20
	2	0.0551	0.0247	0.45	0.4051	>0.50
	3	0.0515	0.0617	1.20	0.9281	0.038
	4	0.0713	0.0691	0.97	0.9759	0.011
Cambridge	1	0.0316	0.0328	1.04	0.9784	>0.50
	2	0.0719	0.1062	1.48	0.9248	0.040
	3	0.0238	0.0246	1.03	0.6858	0.16
	4	0.0705	0.0504	0.72	0.6198	0.19

0.95 in five of the eight blocks. The ratios $\hat{\beta}/\hat{\beta}_b = 1.20$ in block 3 of the Dayton data and $\hat{\beta}/\hat{\beta}_b = 1.48$ in block 2 of the Cambridge data are excessive. These ratios are indicative of a serious problem in the contemplated statistical analysis that requires a documented explanation and, if necessary, remedial action. The facile explanation for these predominantly high ratio values is that Method 6 lacks any substantial laboratory bias. But this explanation runs counter to all collaborative test experience. A more likely explanation is that the true SO_2 concentration drifted from run to run in some of the blocks. This second explanation can be tested by comparing the mean of the four collaborators' Method 6 values for each run against the SO_2 monitoring technique employed at that test site. This comparison is shown in Table B-6. An Envirometrics SO_2 monitor was employed at the Dayton site. Two techniques were used at Cambridge—Walden's theoretical calculation of the SO_2 concentration and a Dynasciences SO_2 monitor. Walden reports that the theoretical calculated values are preferable for comparison purposes, with the Dynasciences monitor readings serving primarily as indicators of the fluctuation in the SO_2 concentration during each run. Table B-6 shows fairly strong positive correlations between the Method 6 mean and the appropriate monitoring technique in several blocks, especially block 3 at Dayton and block 2 at Cambridge. These correlations indicate the existence of sufficient drift in the true SO_2 concentration during some blocks that it was readily detectable by several independent measurement techniques. The actual correlation coefficient r_B between the Method 6 run mean and the appropriate monitoring technique over the four samples comprising a block is shown for all eight blocks in Table B-5. The significance of these block correlation coefficients was determined with a one-sided test using the standard test statistic $r_B\sqrt{n-2}/\sqrt{1-r_B^2}$ which has the t distribution with $n-2$ degrees of freedom[9], where $n = 4$. As Table B-5 shows, blocks 3 and 4 at Dayton and block 2 at Cambridge all possess significant correlations. The logical inference is that the true SO_2 concentration did indeed drift significantly from run to run in these three blocks.

The existence of substantial drift in the true SO_2 concentration invalidates the within-laboratory analysis given in Tables B-3 and B-4 and the within-laboratory coefficient of variation estimates $\hat{\beta}$ presented in Table B-5. The problem now is to decide which blocks contain substantial true drift and how to adjust the data in such blocks so as to permit a meaningful within-laboratory analysis.

Table B-6. Within-Block Drift Comparison: Method 6 Versus Monitoring and Calculation Methods

Site	Block	SO_2 Concentration, 10^{-7} lb/scf				
		Sample	Method 6 Run Mean	Environmetrics Monitor	Walden Calculation	Dynasciences Monitor
Dayton	1	1	823.5	745		
		2	871.5	798		
		3	798.5	696		
		4	855.2	696		
	2	11	588.7	497		
		12	573.5	505		
		13	569.7	522		
		14	582.0	528		
	3	15	183.2	174		
		16	180.7	166		
		17	175.2	162		
		18	166.2	157		
	4	25	1009.0	903		
		26	1097.5	961		
		27	1161.0	1002		
		28	1082.5	969		
Cambridge	1	4	149.2		168	157–166
		5	144.5		179	166–190
		6	148.0		173	190
		7	145.7		177	157
	2	8	479.0		513	472–497
		9	550.7		642	472–513
		10	572.5		670	563
		11	593.8		644	638–696
	3	18	830.5		945	853–903
		19	816.5		895	894
		20	820.5		931	903
		21	843.8		938	927
	4	29	1032.7		1190	1192–1226
		26	973.5		1140	1226–1242
		27	1039.0		1204	1217–1250
		28	989.5		1207	1217–1267

The decision rule utilized to determine which blocks of four runs were plagued with a drifting true SO_2 concentration requires that both of these criteria be met:

(1) The coefficient of variation ratio $\hat{\beta}/\hat{\beta}_b$ for the block is greater than the reasonable upper limit of 0.95;

(2) The correlation coefficient r_B between the Method 6 run means and the run monitor readings for the block is significant at the 0.05 level (i.e., there is less than one chance in twenty that this high a positive correlation would occur by chance).

A perusal of Table B-5 reveals that both of these criteria are met by blocks 3 and 4 of the Dayton data and by block 2 of the Cambridge data. Thus the data obtained by each collaborator on

each run in these three blocks will have to be adjusted for the true drift that occurred in order to achieve a valid within-laboratory analysis.

The data adjustment technique that was used in these three blocks was to adjust each collaborator's value in a run by the amount necessary to give the run the same mean as the block. Thus, the Method 6 mean of each run in these adjusted blocks is the same. Since it is very probable that the Method 6 run mean is at least a good proportional estimate of the true SO_2 concentration, this data adjustment technique should remove most, if not all, the true drift inherent in the corrected data for these blocks. The data adjustment formula used was

$$Y_{ij} = X_{ij} + (\overline{X}_{.j} - \overline{X}_{..})$$

where X_{ij} is the corrected data value and Y_{ij} is the adjusted data value for collaborator i on run j, $\overline{X}_{.j}$ is the run j mean and $\overline{X}_{..}$ is the block mean. The adjusted data used for the within-laboratory analysis is shown in Tables B-7 and B-8 for the Dayton and Cambridge data, respectively. The adjusted data points are denoted by a † following their value. Tables B-9 and B-10 present the within-laboratory analysis of this adjusted data. The $\hat{\beta}/\hat{\beta}_b$ ratios of the three adjusted blocks are reduced from 1.20, 0.97, and 1.48 for the corrected data to 0.76, 0.41, and 0.72 for the adjusted data. So the adjusted data are certainly more reasonable. Furthermore, the data comparisons performed in Section B-5 imply that the adjusted data obtained are the proper data on which to base the within-laboratory precision analysis.

B.4 Relationship of the Standard Deviation to the Mean

In order to analyze the collaborative test data according to the coefficient of variation approach, it is first necessary to justify the fundamental assumption of that approach; namely, that the precision standard deviations of Method 6 are actually proportional to the true concentration value. The basic precision standard deviations for which the proportional relationship must be verified are the between-laboratory (run) standard deviation and the within-laboratory (collaborator block) standard deviation. This section will present the necessary verification data for these two standard deviation relationships.

The direct evidence for proportionality comes from plotting and regressing the pertinent standard deviation versus mean data. The values of the between-laboratory standard deviations and means for each run are presented in the run summaries of Tables 2 and 3 (main report) on the corrected collaborative test data with replacements. Figure B-1 is a plot of this between-laboratory data. Despite the considerable scatter inherent in this plot because of the necessary limitation of the collaborative study to only four collaborators, a proportional relationship, in which the between-laboratory standard deviation of a run increases as the mean of the run increases, appears likely. To classify the relationship, stepwise multiple linear regression through the origin was performed on this between-laboratory data. The potential regressor variables provided to fit the standard deviation s_j as a function of the mean $\overline{X}_{.j}$ were $\overline{X}^{-1}$, $\overline{X}^{1/4}$, $\overline{X}^{1/2}$, $\overline{X}^{3/4}$, $\overline{X}$, $\overline{X}^{5/4}$, $\overline{X}^{3/2}$, $\overline{X}^{2}$, and log $\overline{X}$. The power function $\hat{s}_j = 0.01099\overline{X}_{.j}^{5/4}$ has a 0.9011 correlation with s_j, while the linear function $\hat{s}_j = 0.05992\overline{X}_{.j}$ has a slightly lower correlation of 0.8997. The other simple and multiple regressions are all inferior to these two. Because of the scatter in the data, the exact functional between-laboratory relationship remains uncertain. But the proportional linear relationship appears to be among the best.

Shown in Tables B-9 and B-10 are the within-laboratory standard deviation and mean values calculated for each collaborative laboratory in each block from the corrected Method 6 collaborative test data adjusted for true drift. These within-laboratory data are plotted as Figure B-2. Again

Table B-7. The Corrected Dayton Collaborative Test Data with Replacements, Adjusted for True Drift

METHOD: METHOD 6 --- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CORRECTED SO2 CONC. AT STD. COND. ADJUSTED FOR TRUE DRIFT, 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: DAYTON

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104

INTER-LABORATORY RUN SUMMARY

		LAB 101		LAB 102		LAB 103		LAB 104		RUN SUMMARY		
RUN	SAMPLE	DATA	PORT	DATA	PORT	DATA	PORT	DATA	PORT	MEAN	STD DEV	COEF OF VAR
1	1	729.	(B)	998.	(C)	903.	(A)	719.	(D)	823.5	119.9	.1999
2	2	912.	(C)	929.*	(D)	914.	(B)	736.	(A)	871.5	90.5	.1038
3	3	789.	(D)	819.	(A)	928.	(C)	763.	(B)	798.5	28.6	.0359
4	4	865.	(A)	910.*	(B)	860.	(D)	786.	(C)	855.2	51.9	.0600
5	11	595.	(C)	602.*	(D)	600.	(B)	558.	(A)	588.7	20.7	.0352
6	12	612.	(D)	584.	(A)	572.	(C)	526.	(B)	573.5	35.8	.0625
7	13	586.	(A)	583.*	(B)	582.	(D)	528.	(C)	569.7	27.9	.0489
8	14	588.	(B)	607.	(C)	599.	(A)	539.	(D)	582.0	32.9	.0566
9	15	168.†	(D)	196.†	(A)	176.†	(C)	165.†	(B)	176.2	14.0	.0792
10	16	178.†	(A)	168.†	(B)	181.†	(D)	180.†	(C)	176.7	6.0	.0337
11	17	171.†	(B)	183.†	(C)	181.†	(A)	170.†	(D)	176.2	6.7	.0380
12	18	167.†	(C)	189.†	(D)	178.†	(B)	176.†	(A)	176.2	7.0	.0400
13	25	1118.†	(A)	1198.†	(B)	1115.†	(D)	967.†	(C)	1087.0	81.4	.0749
14	26	1050.†	(B)	1192.†	(C)	1132.†	(A)	976.†	(D)	1087.5	99.9	.0868
15	27	1097.†	(C)	1136.†	(D)	1103.†	(B)	1016.†	(A)	1088.0	51.0	.0468
16	28	1095.†	(D)	1089.†	(A)	1152.†	(C)	1019.†	(B)	1087.5	56.6	.0521

COLLABORATOR SUMMARY

COLLABORATOR	LAB 101	LAB 102	LAB 103	LAB 104
MEAN	670.0	709.2	692.2	613.1
STD. DEVIATION	350.3	371.9	369.2	311.7

PORT SUMMARY

PORT	A	B	C	D
MEAN	670.7	663.1	680.6	665.1
STD. DEVIATION	347.3	350.7	361.6	348.1

*Replacement value.
†Value adjusted for true drift.

Table B-8. The Corrected Cambridge Collaborative Test Data with Replacements, Adjusted for True Drift

METHOD: METHOD 6 --- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CORRECTED SO2 CONC. AT STD. COND. ADJUSTED FOR TRUE DRIFT, 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: CAMBRIDGE

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104

INTER-LABORATORY RUN SUMMARY

		LAB 101		LAB 102		LAB 103		LAB 104		RUN SUMMARY		
RUN	SAMPLE	DATA	PORT	DATA	PORT	DATA	PORT	DATA	PORT	MEAN	STD DEV	COEF OF VAR
1	4	139.	(D)	153.	(B)	155.	(C)	150.	(A)	149.2	7.1	.0478
2	5	142.*	(A)	146.	(C)	143.	(D)	147.	(B)	144.5	2.4	.0165
3	6	152.	(B)	136.	(D)	151.	(A)	143.	(C)	148.0	9.2	.0287
4	7	143.*	(C)	143.	(A)	150.	(B)	147.	(D)	145.7	3.4	.0234
5	8	482.†	(A)	583.†	(C)	559.†	(D)	572.†	(B)	549.0	45.7	.0833
6	9	595.†	(B)	566.†	(D)	519.†	(A)	520.†	(C)	548.7	38.6	.0703
7	10	592.†	(C)	586.†	(A)	533.†	(B)	537.†	(D)	549.5	25.6	.0468
8	11	548.†	(D)	584.†	(B)	504.†	(C)	559.†	(A)	548.7	33.4	.0609
9	18	847.	(B)	826.	(D)	844.	(A)	805.	(C)	830.5	19.4	.0233
10	19	807.	(C)	838.	(A)	812.	(B)	809.	(D)	816.5	14.5	.0177
11	20	837.	(D)	824.	(B)	787.	(C)	834.	(A)	820.5	23.0	.0280
12	21	862.	(A)	850.	(C)	838.	(D)	825.	(B)	843.8	15.4	.0188
13	24	940.	(C)	1123.	(A)	1061.	(B)	1007.	(D)	1032.7	77.4	.0754
14	26	990.	(D)	882.	(B)	1061.	(C)	961.	(A)	973.5	74.1	.0761
15	27	1020.*	(A)	1086.	(C)	1053.	(D)	997.	(B)	1039.0	38.4	.0374
16	28	990.	(B)	899.	(D)	1070.	(A)	999.	(C)	989.5	70.1	.0709

COLLABORATOR SUMMARY

COLLABORATOR	LAB 101	LAB 102	LAB 103	LAB 104
MEAN	627.2	639.7	639.7	625.7
STD. DEVIATION	333.2	336.3	351.7	329.4

PORT SUMMARY

PORT	A	B	C	D
MEAN	642.4	632.7	629.4	627.7
STD. DEVIATION	351.4	327.1	339.4	331.6

*Replacement value.
†Value adjusted for true drift.

Table B-9. Within-Laboratory Analysis of Corrected Dayton Collaborative Test Data with Replacements Adjusted for True Drift

METHOD: METHOD 6 --- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CORRECTED SO2 CONC. AT STD. COND. ADJUSTED FOR TRUE DRIFT, 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: DAYTON

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104

INTRA-LABORATORY COLLABORATOR BLOCK SUMMARY

BLOCK	MEAN	COLLABORATOR		MEAN	STD DEV	COEF OF VAR
1	837.2					
		1	LAB 101	823.7	81.0	.0983
		2	LAB 102	899.0	58.8	.0654
		3	LAB 103	876.2	39.7	.0453
		4	LAB 104	749.7	31.4	.0419
2	578.5					
		1	LAB 101	595.2	11.8	.0198
		2	LAB 102	599.0	12.3	.0207
		3	LAB 103	588.2	13.6	.0232
		4	LAB 104	536.5	14.7	.0275
3	176.4					
		1	LAB 101	171.0	5.0	.0290
		2	LAB 102	182.7	11.5	.0628
		3	LAB 103	174.0	2.4	.0137
		4	LAB 104	178.7	6.6	.0382
4	1087.5					
		1	LAB 101	1090.0	28.6	.0263
		2	LAB 102	1191.2	92.3	.0371
		3	LAB 103	1125.5	21.3	.0189
		4	LAB 104	993.2	25.4	.0256

Table B-10. Within-Laboratory Analysis of Corrected Cambridge Collaborative Test Data with Replacements Adjusted for True Drift

METHOD: METHOD 6 --- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CORRECTED SO2 CONC. AT STD. COND. ADJUSTED FOR TRUE DRIFT, 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: CAMBRIDGE

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104

INTRA-LABORATORY COLLABORATOR BLOCK SUMMARY

BLOCK	MEAN	COLLABORATOR		MEAN	STD DEV	COEF OF VAR
1	196.9					
		1	LAB 101	199.0	5.6	.0389
		2	LAB 102	197.0	4.2	.0289
		3	LAB 103	199.7	5.0	.0333
		4	LAB 104	196.7	2.9	.0196
2	599.0					
		1	LAB 101	591.7	46.3	.0856
		2	LAB 102	579.7	9.3	.0160
		3	LAB 103	527.5	29.2	.0459
		4	LAB 104	597.0	29.1	.0422
3	827.8					
		1	LAB 101	838.2	23.2	.0277
		2	LAB 102	834.5	12.0	.0144
		3	LAB 103	820.2	26.2	.0319
		4	LAB 104	818.2	13.6	.0166
4	1008.7					
		1	LAB 101	985.0	33.2	.0337
		2	LAB 102	997.5	124.7	.1250
		3	LAB 103	1061.2	6.9	.0065
		4	LAB 104	991.0	20.5	.0206

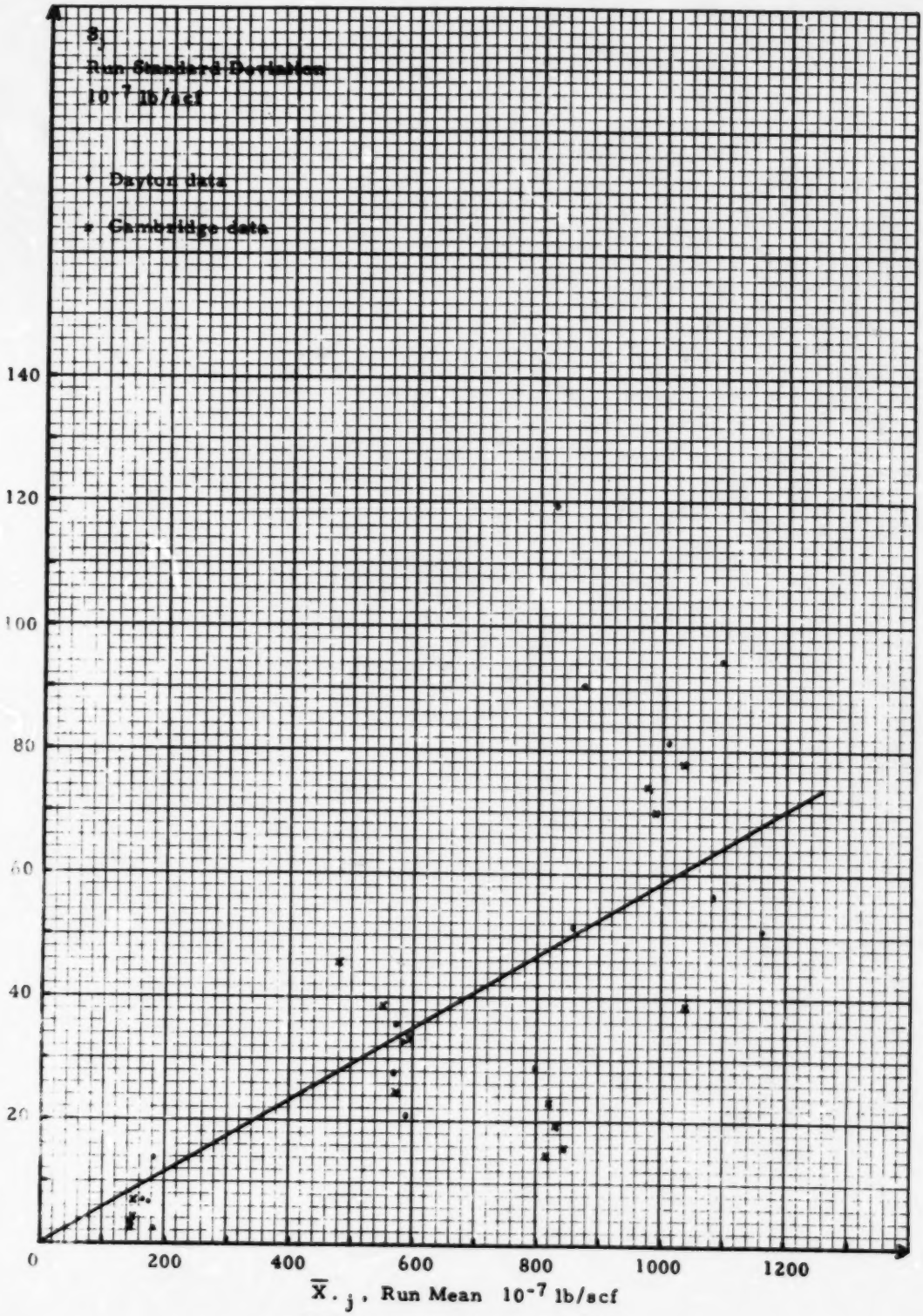

Figure B-1. Between-Laboratory Run Plot

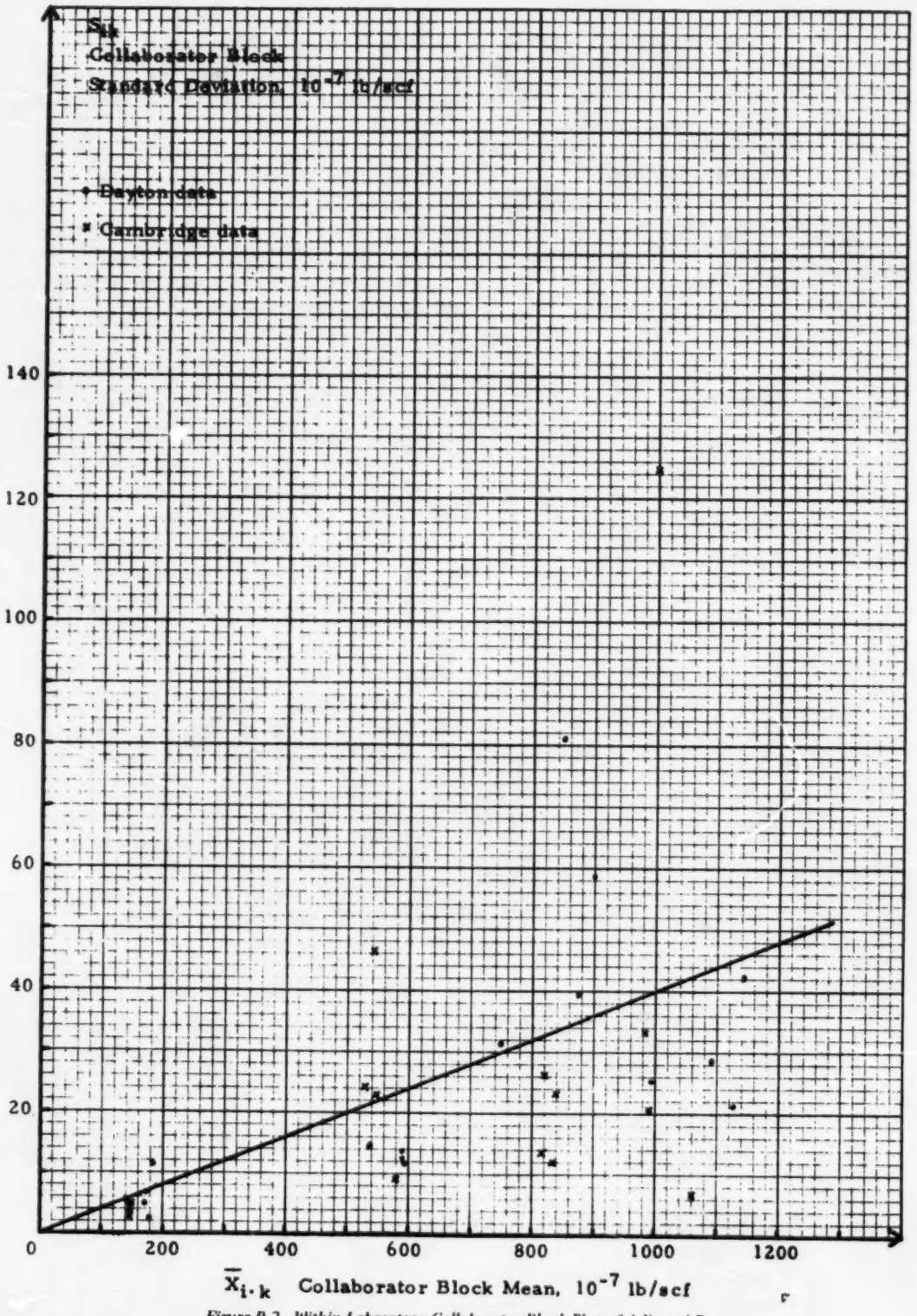

Figure B-2. Within-Laboratory Collaborator Block Plot of Adjusted Data

despite the scatter, a proportional linear relationship appears as good as any other. Stepwise multiple linear regression through the origin of the within-laboratory standard deviation s_{ik} as a function of the mean $\overline{X}_{i,k}$ was conducted on the same set of regressor variables listed above. The proportional linear function $\hat{s}_{ik} = 0.03774\overline{X}_{i,k}$ with a correlation of 0.7880 proved to be the best.

Indirect evidence regarding the proper relationship of the between-laboratory standard deviation to the mean over the Method 6 runs is obtained from Bartlett's test for equality of variance.[10] This test was used to evaluate the linear (no transformation of X), the logarithmic ($\log_{10} X$), and the square root ($\sqrt{X}$) transformations as means of achieving equality of the between-laboratory run variances of the corrected collaborative test data with replacements. The Bartlett's test results are shown in Table B-11. The logarithmic transformation yields far better equality of run variance than either the linear or the square root transformations. However, even under the logarithmic transformation, there is only a 1.7-percent chance that an actual underlying equality of run variance process would have produced data with as much scatter in the between-laboratory run variances as that observed in the Method 6 collaborative test data. Yet the logarithmic transformation is the best transformation available; it is markedly superior to no data transformation at all. In the previous Method 7 collaborative test report[11], it was demonstrated that when the logarithmic transformation of a set of data yields equality of variance (so that the data probably have a lognormal underlying distribution), then the standard deviation is proportional to the mean. The Bartlett's test results shown in Table B-11 indicate that the logarithmic transformation is the transformation of the Method 6 collaborative test run data which best provides equality of the between-laboratory variance. Thus, by the above theorem, the Method 6 between-laboratory standard deviation is proportional to the mean of the run's Method 6 collaborator values.

Table B-11. Adequacy of Transformations to Achieve Equality of Run Variance

Transformation	Bartlett's Test Result	Significance
Linear: $y = x$	$B = 120.1$	$Pr\{\chi^2(31) \geq 120.1\} << 0.0001$
Logarithmic: $y = \log_{10}(x)$	$B = 49.9$	$Pr\{\chi^2(31) \geq 49.9\} = 0.017$
Square root: $y = \sqrt{x}$	$B = 79.5$	$Pr\{\chi^2(31) \geq 79.5\} < 0.0001$

The preceding evidence provides the basis for drawing conclusions regarding the true nature of the between-laboratory standard deviation σ_b and the within-laboratory standard deviation σ of Method 6. From both the direct graphical-regression evidence and the indirect equality of variance conclusions gained from the Method 6 run data, the natural inference is that the underlying between-laboratory standard deviation for a run is proportional to the run's true SO_2 concentration μ: $\sigma_b = \beta_b\mu$. It is also proper to conclude that the underlying within-laboratory standard deviation σ over runs sampled by a laboratory at the same true SO_2 concentration μ is proportional to that concentration: $\sigma = \beta\mu$. This latter conclusion is based primarily on the plot (Figure B-2) and on the regression of the within-laboratory collaborator block data adjusted for true drift. Supporting evidence for the $\sigma = \beta\mu$ coefficient of variation relationship derives from the prior conclusion that $\sigma_b = \beta_b\mu$, because since $\sigma_b^2 = \sum \sigma_i^2$, it is probable that the component σ^2 would behave like its aggregate σ_b^2.

Incidentally, Bartlett's test for equality of run variance was originally applied to the corrected collaborative test data, and its logarithmic and square root transformations, with the seven missing and erroneous data points removed (cf. Tables 2 and 3). Results very similar to those reported in Table B-11 were obtained. Hence, the logarithmic transformed corrected data were utilized as the proper basis for deriving the seven replacement values denoted by asterisks in Tables 2 and 3 for the seven points considered as missing. Minimum variance unbiased estimates for each of these seven missing points were obtained by the following procedure applied to the logarithmic transformed data. "Call the laboratory missing a value on a run the missing laboratory. Compute the missing

laboratory's average difference from the other laboratories' run means over all the complete runs in the block. Add this average difference to the mean of the other laboratories' values on the missing point run to give the minimum variance unbiased estimate of the point in the transformed scale. Convert this value back to the original scale and use it to replace the missing point's value." An example, the erroneous value reported by Lab 102 in Sample 4 of block 1 of the Dayton test data, should serve to clarify this procedure. The complete runs in block 1 are for Samples 1 and 3. The Lab 102 average of the logarithmic values for Samples 1 and 3 is 2.9437. The average of the other laboratories' sample means for these runs is 2.9071. The average difference for Lab 102 in block 1 is thus + 0.0366. The mean of the Lab 101, Lab 103, and Lab 104 values for Sample 4 is 2.9223. Then the transformed replacement value for Lab 102 in Sample 4 is 2.9223 + 0.0366 = 2.9589. The antilog of 2.9589 is 910. Thus, 910 is the replacement value for Lab 102 on Sample 4 of the Dayton data. All seven replacement values are shown in Tables 2 and 3 (main report) followed by an asterisk.

B.5 Component Standard Deviation, Repeatability and Reproducibility Estimation

In this section, the standard deviations associated with the relevant variance components of a Method 6 SO_2 concentration determination c are estimated from the Dayton and Cambridge collaborative test and gas cylinder test data. Also estimated are the repeatability and reproducibility of a Method 6 test result T, in which the value is defined as the average of three repetitions, each of which consists of two Method 6 determinations:

$$t = \frac{1}{3}\sum_{r=1}^{3}\left(\frac{1}{2}\sum_{i=1}^{2} c_{ri}\right) = \frac{1}{6}\sum_{1}^{6} c_{ri}$$

where c_{ri} is the Method 6 SO_2 concentration obtained on determination i of repetition r. This test result is artificial in that three repetitions of the emissions rate $Q_s\bar{c}_{r.}$, where Q_s is the experimental volumetric flow rate determined by Method 2, are actually used instead of t to determine sulfur dioxide performance test compliance.[12] Yet T is a very useful artificial construct because it permits assessment of the relative importance of the repeatability component versus the laboratory bias component in Method 6 reproducibility under the regulated field sampling situation in which Method 6 will be employed. Throughout this section, calculation formulas are presented for computing statistics. These calculation formulas were derived in the prior Method 7 test report[13] under the identical coefficient of variation underlying situation shown in Section B.4 to exist in the Method 6 collaborative tests.

First, estimates will be derived from the Dayton and Cambridge Method 6 collaborative test data. The within-laboratory coefficient of variation β is estimated from the 32 collaborator block coefficient of variation point estimates $s_{ik}/\bar{X}_{i.k}$ shown in Tables B-9 and B-10 for the corrected data with replacements adjusted for true drift:

$$\hat{\beta} = \frac{\alpha_4}{32}\sum_{1}^{32}(s_{ik}/\bar{X}_{i.k}) = \frac{1.0854}{32}\,[1.180373] = 0.040037$$

So the within-laboratory standard deviation estimate of a Method 6 determination c is $\hat{\sigma} = \hat{\beta}c = 0.040037c$. The between-laboratory coefficient of variation is similarly estimated from the 32 run coefficient of variation point estimates shown in Tables 2 and 3 (main report) for the

corrected data with replacements:

$$\hat{\beta}_b = \frac{\alpha_4}{32} \sum_{j=1}^{32} (s_j / \bar{X}_{.j}) = \frac{1.0854}{32} [1.708541] = 0.057952$$

The laboratory bias coefficient of variation estimate is calculated from $\hat{\beta}$ and $\hat{\beta}_b$:

$$\hat{\beta}_L = \sqrt{\hat{\beta}_b^2 - \hat{\beta}^2} = \sqrt{(0.057952)^2 - (0.040037)^2} = 0.041898$$

Thus the laboratory bias standard deviation estimate is $\hat{\sigma}_L = \hat{\beta}_L c = 0.041898c$. The repeatability standard deviation of a Method 6 test result is estimated as

$$\hat{\sigma}/\sqrt{m} = (0.040037\ t)/\sqrt{6} = 0.016345\ t$$

The repeatability standard deviation estimate has $\phi = pg(n-1) = 4 \cdot 8 \cdot (4-1) = 96$ degrees of firmness. Hence, the percentage uncertainty standard deviation of the repeatability standard deviation estimate is

$$\%CV_{\hat{\sigma}/\sqrt{m}} = 100 \sqrt{\frac{1}{2\phi}} = 100 \sqrt{\frac{1}{192}} = 7.22\%$$

Thus the 95 percent confidence interval for the repeatability standard deviation of a Method 6 test result is given by

$$0.016345\ t \pm 1.96\ (0.0722)(0.016345\ t) = 0.016345\ t \pm 0.002312\ t = (0.01403\ t, 0.01866\ t)$$

The reproducibility standard deviation estimate of a Method 6 test result is

$$\sqrt{\hat{\sigma}_L^2 + \hat{\sigma}^2/m} = \sqrt{(0.041898\ t)^2 + (0.040037\ t)^2/6} = 0.044974\ t$$

The degrees of firmness in this reproducibility standard deviation estimate are

$$\phi = \frac{(ng)^2(\gamma + 1/m)^2}{\dfrac{(ng-m)^2}{pg(n-1)m^2} + \dfrac{(1+ng\gamma)^2}{p-1}} = \frac{(4 \cdot 8)^2\ (1.095 + 1/6)^2}{\dfrac{(4 \cdot 8 - 6)^2}{4 \cdot 8 \cdot 3 \cdot 6^2} + \dfrac{(1 + 4 \cdot 8 \cdot 1.095)^2}{3}} = 3.763$$

where $\hat{\gamma} = (\hat{\sigma}_L/\hat{\sigma})^2 = (0.041898\ \mu/0.040037\mu)^2 = 1.095$. So the percentage uncertainty standard deviation of the reproducibility standard deviation estimate is

$$\%CV_{\sqrt{\hat{\sigma}_L^2 + \hat{\sigma}^2/m}} = 100 \sqrt{\frac{1}{2\phi}} = 100 \sqrt{\frac{1}{7.526}} = 36.45\%$$

Therefore, the 95 percent confidence interval for the reproducibility standard deviation of a Method 6 test result is

$$0.044974\ t \pm 1.96\ (0.3645)\ (0.044974\ t) = 0.044974\ t \pm 0.032130\ t = (0.01284\ t, 0.07710\ t)$$

In Mandel's system[14], the terms repeatability and reproducibility represent the maximum allowable deviation that could occur between two test results if the test results are to be considered consistent with each other at the 95-percent confidence level:

$$\text{Repeatability} = 2.77 \cdot \hat{o}/\sqrt{m} = 2.77(0.016345\ \bar{t}) = 0.04528\ \bar{t}$$

$$\text{Reproducibility} = 2.77\sqrt{\hat{o}_L^2 + \hat{o}^2/m} = 2.77(0.044974\ \bar{t}) = 0.12458\ \bar{t}$$

The values calculated in this paragraph are the precision estimates for Method 6 derived from the corrected collaborative test data at the Dayton and Cambridge sites.

One can also derive alternative Method 6 precision estimates from the corrected gas cylinder test data. The gas cylinder precision estimates calculated below for Method 6 serve to confirm the estimates obtained from the collaborative test data:

$$\hat{\beta} = \frac{1.0854}{23}[0.940948] = 0.044405$$

$$\hat{o} = 0.044405\ c$$

$$\hat{\beta}_b = \frac{1.0854}{24}[1.382856] = 0.062540$$

$$\hat{\beta}_L = \sqrt{(0.062540)^2 - (0.044405)^2} = 0.044039$$

$$\hat{o} = 0.044039\ c$$

$$\hat{o}/\sqrt{m} = 0.044405\ t/\sqrt{6} = 0.018128\ t$$

$$\sqrt{\hat{o}_L^2 + \hat{o}^2/m} = \sqrt{(0.044039\ t)^2 + (0.044405\ t)^2/6} = 0.047624\ t$$

The gas cylinder data give slightly higher precision estimates for Method 6 than does the collaborative test data. However, when one considers the uncertainty computed in the repeatability and reproducibility estimates above, it is remarkable that the gas cylinder precision estimates agree so well with the collaborative test precision estimates. If the four collaborative laboratories participating in the Method 6 collaborative tests at Dayton and Cambridge are indeed representative of the population of laboratories that will perform Method 6 with respect to their adherence to and execution of the method, then the Method 6 precision estimates derived from the collaborative test data are probably quite accurate. Note also that the ratio $\hat{o}/\hat{o}_L$ has the value 0.956 from the collaborative test estimates and the value 1.008 from the gas cylinder test estimates. When the sensitivity of the ratio $\hat{o}/\hat{o}_L$ is taken into account, the closeness of these values confirms the validity of the adjustment procedure used in Section B.3 to modify the corrected collaborative test data with replacements prior to estimating $\hat{o}$. The Method 6 precision estimates calculated both from the collaborative test data and from the gas cylinder test data are summarized in Table 7 (main report).

B.6 Analysis of the Unknown Sulfate Solution Test Data

An unknown sulfate solution test was conducted as part of the Method 6 collaborative study to isolate the accuracy and the precision of the analytical phase of Method 6. 10-mℓ samples of four

sulfate solutions, labeled Solution A, Solution B, Solution C, and Solution D, in which the concentrations were unknown to the collaborative laboratory teams, were analyzed in triplicate on each of three days in conjunction with the collaborative test and gas cylinder data by each collaborative team along with both sites' data. Figure 8 (body of report) which is a copy of the instruction and reporting form, suggests the data layout. The unknown solution, the collaborator C, and the site S of the concurrently analyzed samples are crossed factors in the full factorial design. The day factor $D(CS)$ is nested within $C \times S$, and the replicate factor $R(CSD)$ is nested within days.

All the reported unknown sulfate solution test data is presented in Table B-12. Table B-13 is a summary of the Table B-12 data averaged over replicates and days to show the collaborator and site interaction effects. A site comparison of the Table B-13 data by collaborator is interesting. Lab 101

Table B-12. Reported Sulfate Solution Concentrations, 10^{-7} lb SO_2/scf

Collaborator	Day	Repl.	With Dayton Samples				With Cambridge Samples			
			Sol. A	Sol. B	Sol. C	Sol. D	Sol. A	Sol. B	Sol. C	Sol. D
Lab 101	1	1	349	−0.30	528	174	357	0.0	525	173
		2	349	−0.70	528	174	353	1.6	527	167
		3	349	−0.70	527	173	353	1.6	527	173
	2	1	349	−0.90	530	172	352	0.0	533	173
		2	349	−0.30	529	173	352	1.7	534	177
		3	349	0.00	531	174	351	2.3	533	176
	3	1	351	−1.00	530	173	353	0.0	538	174
		2	350	−1.30	529	174	353	0.0	528	172
		3	350	0.00	531	175	351	−1.7	531	174
Lab 102	1	1	348	0.99	525	177	348	0.0	515	174
		2	348	1.07	518	179	346	0.0	517	173
		3	352	0.87	520	174	344	0.0	516	167
	2	1	337	0.94	500	167	343	0.0	517	196
		2	351	0.88	509	170	350	0.0	520	192
		3	344	0.88	511	169	343	0.0	527	177
	3	1	373	0.70	509	172	342	0.0	514	177
		2	366	0.31	512	171	343	0.0	509	173
		3	340	0.31	522	175	345	0.0	518	176
Lab 103	1	1	350	0.0	524	178	337	0.0	506	171
		2	350	0.0	526	176	338	0.0	504	169
		3	352	0.0	524	176	340	0.0	506	169
	2	1	352	0.0	524	176	338	0.0	507	172
		2	348	0.0	526	174	337	0.0	506	169
		3	352	0.0	526	176	337	0.0	506	171
	3	1	348	0.0	524	174	337	0.0	504	171
		2	348	0.0	524	174	338	0.0	506	169
		3	350	0.0	526	176	338	0.0	506	171
Lab 104	1	1	352	0.0	522	166	361	0.0	535	181
		2	352	0.0	517	169	363	0.0	535	180
		3	347	0.0	512	169	359	0.0	535	178
	2	1	345	0.0	518	174	356	0.0	534	180
		2	346	0.0	518	174	354	0.0	536	181
		3	347	0.0	515	173	356	0.0	536	180
	3	1	346	0.0	523	171	359	0.0	544	183
		2	345	0.0	520	173	361	0.0	541	181
		3	346	0.0	520	169	358	0.0	532	183

Table B-13. Sulfate Solution Concentrations Averaged Over Days, 10^{-7} lb SO_2/scf

Collaborator	With Dayton Samples				With Cambridge Samples			
	Sol. A	Sol. B	Sol. C	Sol. D	Sol. A	Sol. B	Sol. C	Sol. D
Lab 101	349.4	−0.58	529.2	173.6	352.8	0.61	530.7	173.2
Lab 102	351.0	0.77	514.0	172.7	344.9	0.00	517.0	178.3
Lab 103	350.0	0.00	524.9	175.6	337.8	0.00	505.7	170.2
Lab 104	347.3	0.00	518.3	170.9	358.6	0.00	536.4	180.8

shows little variation, except for Solution B, between the two sites. Lab 102 shows more variation, but there is no consistent site pattern over the four solutions. However, Lab 103 obtained consistently lower determinations with its Cambridge samples than with its Dayton samples, while Lab 104 obtained consistently higher determinations with its Cambridge site samples. It is noteworthy that Labs 101 and 104 had the same chemist analyzing both sites' samples, while Labs 102 and 103 used one analyst for the Dayton site samples and a different analyst for the Cambridge site samples. Table B-14 is a further summarization of the Table B-12 data in which the two sites' data are also averaged to show only the laboratory effects. Lab 103 appears to have a low laboratory bias in Table B-14, but it can be seen from Table B-13 that only the analysis of the Cambridge site samples is responsible for this apparent bias.

Table B-14. Average Laboratory Sulfate Solution Concentrations, 10^{-7} lb SO_2/scf

Collaborator	Solution A	Solution B	Solution C	Solution D
Lab 101	351.1	0.02	529.9	173.4
Lab 102	347.9	0.39	515.5	175.5
Lab 103	343.9	0.00	515.3	172.9
Lab 104	352.9	0.00	527.4	175.8
Prepared SO_2 Concentration	352.50	0.00	528.75	176.25

A separate analysis of variance was performed on the data for each of the four unknown sulfate solutions that are displayed in Table B-12. Based on a random effects model, the four analyses of variance and their variance components are presented in Table B-15. The significance of the variance components for each unknown solution is shown in Table B-16. Clearly the collaborator C (i.e., pure laboratory bias) and the site S factors have no significant effect on the analytical phase of Method 6 at any SO_2 concentration level in the working range. However, the collaborator site interaction factor CS has a very significant effect ($P \leq 0.014$) at all SO_2 concentration levels. This is a result of the interesting collaborator-site data pattern of Table B-13 pointed out in the previous paragraph. The change in the analyst performing the Method 6 analytical phase by Labs 102 and 103, i.e., the operator factor, certainly contributes to the size of the collaborator site interaction effect. Lab 103 showed a uniform marked reduction in Method 6 SO_2 determinations when a different chemist analyzed the Cambridge samples. But the Lab 104 SO_2 determinations for the Dayton samples it analyzed were consistently low, much lower than its Cambridge samples. Lab 104 had the same chemist analyze all of its Method 6 SO_2 samples, both from Dayton and from Cambridge. So another factor in addition to the operator factor must also be responsible for the magnitude of the collaborator site interaction effect. Lab 104 reported uniformly lower SO_2 concentrations using Method 6 on all the samples it analyzed (i.e., the collaborative test data, the gas cylinder data, and the unknown sulfate solution data) from the earlier Dayton test, than from the later Cambridge test (cf. Tables 2, 3, 4, 5, and B-13). A plausible explanation is that the effective normality of the barium perchlorate titrant was inadvertently increased in analysis of the Dayton

Table B-15. Analyses of Variance of Sulfate Solution Data by Concentration

Factor	Sum of Squares	D.F.	Mean Square	Expected Mean Square	Variance Component
Solution B–Mean = 0.101					
C	1.96	3	0.65	$18\sigma^2_C + 9\sigma^2_{CS} + 3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_C = 0$
S	0.20	1	0.20	$36\sigma^2_S + 9\sigma^2_{CS} + 3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_S = 0$
CS	8.85	3	2.95	$9\sigma^2_{CS} + 3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_{CS} = 0.279$
D(CS)	7.06	16	0.44	$3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_D = 0.091$
R(CSD)	8.06	48	0.17	σ^2_R	$\hat{\sigma}^2_R = 0.168$
Solution D–Mean = 174.4					
C	118.3	3	39.4	$18\sigma^2_C + 9\sigma^2_{CS} + 3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_C = 0$
S	110.0	1	110.0	$36\sigma^2_S + 9\sigma^2_{CS} + 3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_S = 0$
CS	603.0	3	201.0	$9\sigma^2_{CS} + 3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_{CS} = 17.70$
D(CS)	667.3	16	41.7	$3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_D = 11.53$
R(CSD)	344.7	48	7.2	σ^2_R	$\hat{\sigma}^2_R = 7.18$
Solution A–Mean = 349.0					
C	850.5	3	283.5	$18\sigma^2_C + 9\sigma^2_{CS} + 3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_C = 0$
S	16.1	1	16.1	$36\sigma^2_S + 9\sigma^2_{CS} + 3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_S = 0$
CS	1440.9	3	480.3	$9\sigma^2_{CS} + 3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_{CS} = 49.84$
D(CS)	508.4	16	31.8	$3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_D = 4.83$
R(CSD)	830.0	48	17.3	σ^2_R	$\hat{\sigma}^2_R = 17.29$
Solution C–Mean = 522.0					
C	3232.6	3	1077.5	$18\sigma^2_C + 9\sigma^2_{CS} + 3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_C = 1.05$
S	12.5	1	12.5	$36\sigma^2_S + 9\sigma^2_{CS} + 3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_S = 0$
CS	3176.2	3	1058.7	$9\sigma^2_{CS} + 3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_{CS} = 113.72$
D(CS)	562.7	16	35.2	$3\sigma^2_D + \sigma^2_R$	$\hat{\sigma}^2_D = 8.25$
R(CSD)	500.0	48	10.4	σ^2_R	$\hat{\sigma}^2_R = 10.42$

Table B-16. Significance of Sulfate Solution Factors

Solution	Factor	F-Ratio	Significance
B	C	0.221	$P > 0.50$
	S	0.066	$P > 0.50$
	CS	6.688	$P = 0.004$
	D(CS)	2.627	$P = 0.005$
D	C	0.196	$P > 0.50$
	S	0.547	$P > 0.50$
	CS	4.820	$P = 0.014$
	D(CS)	5.808	$P < 0.001$
A	C	0.590	$P > 0.50$
	S	0.033	$P > 0.50$
	CS	15.115	$P < 0.001$
	D(CS)	1.838	$P = 0.05$
C	C	1.018	$P \approx 0.50$
	S	0.004	$P > 0.50$
	CS	5.645	$P = 0.008$
	D(CS)	1.125	$P \approx 0.40$

samples. The Lab 104 analyst says that the same flask of titrant was used for both the Dayton and the Cambridge samples. However, he did modify his procedure for filling the burette during sample analysis of all the Cambridge samples. In analyzing the Dayton samples, the titrant was transferred to an intermediate beaker and left standing until needed in titrating each sample to a pink endpoint. Later the analyst realized that the isopropanol would probably evaporate from the standing beaker to yield a higher effective titrant normality. So in analyzing the Cambridge samples, the barium perchlorate titrant was kept in the stoppered flask until needed in the titration step. Since isopropanol will evaporate from an open standing beaker, the Lab 104 procedure change is the likely explanation for the low Method 6 SO_2 concentration determinations it made on all Dayton samples. Thus, uniform analysis procedural variation is another causative factor behind the sizable collaborator site interaction effect.

Table B-16 shows that the day factor D has a significant effect on the analytical phase of Method 6, but only at low SO_2 concentration levels. Based on the large effect of the ostensibly minor Lab 104 procedural change discussed above, it is reasonable to believe that small Method 6 procedural variations made from day to day caused the day effect. Such procedural variations would logically have greater impact on the lower Method 6 SO_2 concentration determinations.

The precision variability measures of the Method 6 analytical phase can be estimated by coefficient of variation analysis. Since the variance component estimates given in Table B-15 for the blank Solution B are very small in comparison with the estimates for the other solutions, the necessary proportionality of standard deviation to mean is a plausible assumption. The within-laboratory standard deviation component $\hat{\sigma}$ is estimated from the replication variance component $\hat{\sigma}_R^2$, while the between-laboratory standard deviation $\hat{\sigma}_b$ is estimated from the between-laboratory mean square

$$MS_b = \frac{1}{18} \sum_{s,d,r=1}^{18} \left[\frac{1}{3} \sum_{c=1}^{4} (X'_{csdr} - \overline{X}_{.sdr})^2 \right]$$

at each of the 18 site, day, replicate combinations for each of the four solutions. As Table B-17 discloses, estimates of $\hat{\beta} = 0.01103$ and $\hat{\beta}_b = 0.02448$ are obtained for the analytical phase of Method 6 from the unknown sulfate solution data by this method. In Table B-18 all the precision variability estimates for the analytical phase of Method 6 are presented as a result of a coefficient of variation analysis.

Table B-17. Analytical Coefficient of Variation

Solution	Mean 10^{-7} lb/scf		Within Laboratory		Between Laboratory	
	True μ	Method 6 $\overline{x}$	Std. Dev., $S = \sqrt{\hat{\sigma}_R^2}$	Beta, $\hat{\beta}$	Std. Dev., $S_b = \sqrt{MS_b}$	Beta, $\hat{\beta}_b$
B	0.00	0.10	0.410		0.639	
D	176.25	174.40	2.680	0.01520	5.161	0.02928
A	352.50	348.97	4.158	0.01180	7.865	0.02231
C	528.75	522.03	3.227	0.00610	11.551	0.02184
				$\overline{\hat{\beta} = 0.01103}$		$\overline{\hat{\beta}_b = 0.02448}$

Table B-18. Method 6 Analytical Phase Precision Variability Estimates

Source of Test Data	Precision Variability Measure	Test Data Version	Component Estimates		Test Result Estimates	
			Coef. of Var., $\hat{\beta}$	Std. Dev., $\hat{\sigma}$	Std. Dev.	Mandel Def.
Unknown Sulfate Solution Test Data	Within Lab	CD	$\hat{\beta} = 0.01103$	$\hat{\sigma} = 0.01103\,c$		
	Between Labs	CD	$\hat{\beta}_b = 0.02448$	$\hat{\sigma}_b = 0.02448\,c$		
	Lab Bias	CD	$\hat{\beta}_L = 0.02185$	$\hat{\sigma}_L = 0.02185\,c$		
	Repeatability (m = 6)	CD			$0.00450\,t$	$0.01247\,t$
	Reproducibility (m = 6)	CD			$0.02231\,t$	$0.06180\,t$

B.7 The Minimum Detectable Limit

The minimum detectable limit of Method 6 is the smallest Method 6 test result value t that is significantly larger than zero in the reproducibility sense. As Table 10 indicates, the reproducibility variance can be partitioned into an analytically induced portion and a field-induced portion. The unknown sulfate solution test, which included repeated analysis of a blank Solution B, provides an excellent means for estimating the actual analytical reproducibility variance at $\mu = 0$. From Table B-17, the analytical reproducibility variance at $\mu = 0$ is estimated as $\hat{\sigma}_L^2 + \hat{\sigma}^2/6 = (s_b^2 - s^2) + s^2/6 = (0.639 - 0.410)^2 + (0.410)^2/6 = 0.2682 \times (10^{-7}\ \text{lb/scf})^2$. Now Table 10 shows that only 24.6 percent of the Method 6 reproducibility variance is caused by the analytical phase in the working Method 6 range where $\sigma = \beta\mu$. While Table B-17 suggests that the analytical phase is responsible for considerably more than 24.6 percent of the variation at $\mu = 0$, we will nevertheless make the conservative assumption that the 24.6 percent figure remains valid. On this assumption, the Method 6 reproducibility variance at $\mu = 0$ is given by $(100\%/24.6\%)\ (0.2682)\ (10^{-7}\ \text{lb/scf})^2 = 1.090 \times (10^{-7}\ \text{lb/scf})^2$. Then the upper 95 percent confidence limit for a true concentration $\mu = 0$ is $C_{.95} = 1.96\sqrt{1.090 \times (10^{-7}\ \text{lb/scf})^2} = 2.05 \times 10^{-7}$ lb/scf. So the minimum detectable limit of a Method 6 test result is 2.05×10^{-7} lb/scf. When a laboratory obtains a Method 6 test result value t as high as 2.05×10^{-7} lb/scf, there is at most a 5-percent chance that the true sulfur dioxide emission concentration was zero.

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